

NANYANG
TECHNOLOGICAL
UNIVERSITY

**ELECTROCHROMIC CARBON NANOTUBE
POLYDIACETYLENE AND ZINC OXIDE HYBRIDS**

REINACK VARGHESE HANSEN
SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING

2016

**ELECTROCHROMIC CARBON NANOTUBE
POLYDIACETYLENE AND ZINC OXIDE HYBRIDS**

REINACK VARGHESE HANSEN

School of Mechanical and Aerospace Engineering

A thesis submitted to Nanyang Technological University
in partial fulfillment of the requirement for the degree of

DOCTOR OF PHILOSOPHY

2016

Acknowledgement

I thank Nanyang Technological University for letting me fulfill my wish of pursuing a PhD here.

I express my sincere gratitude to my supervisor, Dr Yang Jinglei, for his guidance and patience over the last four years. Along with Dr Zheng Lianxi, you have always given me excellent advice and encouragement to mould me into the researcher and the person I am today.

I thank Dr Zhang Yani and Dr Zhan Zhaoyao for teaching me the basic experimental skills and helping me with the experimental set up during the initial stages, without which I would not have been able to design the experiments required for completing this thesis.

To all my group mates, especially Dr Sun Gengzhi, Dr Hari Krishna, Dr An Jianing, Huang Mingyue, Dr Sivarampanicker Sreejith and Dr Tang Xiuzhi, I will be forever grateful for your help and invaluable discussions whenever I was stuck with work.

To Li Zhong, I am extremely thankful for the time and effort you put in to carry out characterization of some of the samples prepared towards this thesis.

I thank all the staff at the Micromachines Lab and Mechanics of Microsystems Lab, where I have carried out most of my work.

Finally, I thank my family, especially my wife, Vijitha Mammen, for helping me get through the stressful times by showing me there is more to life than working throughout and not letting me give up when the going got tough.

Table of Contents

Acknowledgement	I
Table of Contents	III
Table of Figures	IX
List of Tables	XVII
Abstract.....	XIX
Chapter 1 Introduction	1
1.1 Background and motivation.....	1
1.2 Objectives	3
1.3 Scope.....	3
1.4 Outline of the thesis	4
Chapter 2 Literature review	5
2.1 Chromism.....	5
2.2 Types of chromism	5
2.3 Basics of polydiacetylenes.....	8
2.4 PDA Chromism.....	11
2.5 Significance of PDA backbone fluctuations	14
2.5.1 <i>Influence of side groups</i>	15
2.5.2 <i>Influence of π-electrons</i>	18
2.5.3 <i>Influence of head group</i>	20
2.6 Established chromism mechanisms of PDA.....	22

2.6.1 <i>Thermochromism</i>	22
2.6.2 <i>pH chromism</i>	24
2.6.3 <i>Light induced chromism</i>	25
2.7 Making PDA chromism reversible	25
2.7.1 <i>Aromatic interactions</i>	25
2.7.2 <i>Covalent interactions</i>	26
2.7.3 <i>Hydrogen bonds</i>	27
2.7.4 <i>Metal ion effect</i>	28
2.8 Basics of carbon nanotubes.....	30
2.9 From Aligned CNTs to macroscopic assemblies.....	32
2.10 Electron transport in CNT yarns	35
2.11 Foreign molecule interaction with CNTs.....	37
2.11.1 <i>Covalent interactions of molecules with CNT</i>	38
2.11.2 <i>Non-covalent interactions of molecules with CNT</i>	39
2.11.3 <i>Dependence of polymer structure</i>	42
2.12 What we know about CNT-PDA electrochromism	44
Chapter 3 Materials and experiments	46
3.1 Materials	46
3.2 Experiments	46
3.2.1 <i>In-situ absorption spectroscopy</i>	47
3.2.2 <i>In-situ Raman spectroscopy</i>	48

3.2.3 Polarized Raman measurements.....	48
3.2.4 Raman mapping	49
3.3 Material characterization	50
Chapter 4 Growth of drawable CNT Forests and preparation of aligned CNT-PDA Composites	51
4.1 Growth of drawable CNT forests.....	51
4.2 Transferring CNT sheets from forests	54
4.3 Preparing CNT-PDA composites.....	55
4.4 Controlling extent of polymerization of DA.....	56
Chapter 5 A study of electrochromism in CNT-PDA composites	59
5.1 Introduction.....	59
5.2 Current induced morphology changes	61
5.3 The blue to red phase transition.....	64
5.4 Stress in the PDA backbone.....	65
5.5 Evidence for PDA realignment.....	68
5.6 Mechanistic Interpretation	70
5.7 Versatility of CNT-PDA chromism	74
5.8 Summary.....	75
Chapter 6 Dependence of critical transition voltage on interaction between CNT and PDA.....	76
6.1 Introduction.....	76
6.2 Morphology changes due to heating.....	77

6.2.1 Optical microscopy	77
6.2.2 Scanning electron microscopy	78
6.3 Heat induced order in PDA.....	80
6.4 Linking V_c with phase transition dynamics	82
6.5 Effect of heating on current flow	84
6.6 PDA realignment comparison.....	86
6.7 Quantifying interaction between CNT and PDA	89
6.8 Mechanistic interpretation	91
6.9 Summary	94
Chapter 7 Reversible electrochromism in CNT-ZnO-PDA composites	95
7.1 Introduction.....	95
7.2 Morphology and Characterization	96
7.3 Reversibility of phase change in CNT-ZnO-PDA.....	98
7.4 PDA alignment before and after current flow.....	99
7.5 Confirming blue phase recovery in CNT-ZnO-PDA.....	101
7.6 Improved conductivity in CNT-ZnO-PDA.....	103
7.7 Mechanistic interpretation of phase change in CNT-ZnO-PDA.....	104
7.8 Does ZnO alter band gap in the hybrid?	105
7.9 Summary	106
Chapter 8 Conclusions and future work.....	108
8.1 Conclusions.....	108

8.2 Future work.....	109
References.....	111
Biography	129

Table of Figures

Figure 2.1 Classification of types of chromism.	6
Figure 2.2 a) Schematic representation of σ -bonds and pz orbitals in polydienes, b) Peierls distortion in polyacetylene and c) HOMO-LUMO transitions.	9
Figure 2.3 Recent conceptually new developments in PDA applications.	10
Figure 2.4 (a) General structure of diacetylene precursor and (b) topochemical polymerization process of PDA.	11
Figure 2.5 (a) Typical visible spectra of blue and red phases of PDA and (b) Fluorescence spectra.	12
Figure 2.6 (a) Characteristic ratio (C_p) vs degree of polymerization (P_w) and (b) $q^2g(q)$ versus q plot of P3BCMU in DMF.	15
Figure 2.7 (a) and (b) shows polymer chains with and without side groups respectively; (c), (d) and (e) correspond to model for ribbon-like structure with continuous angular deviation.	17
Figure 2.8 Chain folding at low concentration (left) and high concentration (right) of π - electrons.	20
Figure 2.9 (a) Absorption spectrum of PPCDA and (b) PAEPCDA in response to change in pH; (c) PPCDA in high pH region and (d) PAEPCDA in low pH region.	21
Figure 2.10 Thermochromism in PDA through molecular re-organization, metal co- ordination and organic/inorganic hybrid structures.	23
Figure 2.11 Color changes of PDA lipids in presence of HCl or NH_3	24
Figure 2.12 Conformation change induced by azobenzene in PDA resulting in color change.	25
Figure 2.13 Structure showing the strong aromatic links in the polymer resulting from 10,12 DHDP/TC.	26

Figure 2.14 Designed diacetylene silicate species with strong covalent head group links with inorganic silica framework.	27
Figure 2.15 (a) DA monomers with different head groups 1-4 and the chromatic response of resulting PDAs (right) and (b) enhanced H-bonds by incorporating functional groups capable of H-bonding onto conventional PDA.....	28
Figure 2.16 Different modes of interaction of PDA head groups with ZnO surface.	29
Figure 2.17 TEM images of MWCNT (left) and illustration of conversion of graphene sheet to CNT (right).	30
Figure 2.18 (a) Comparison of pyramidalization angle and (b) π -orbital misalignment in CNTs and fullerene C ₆₀	31
Figure 2.19 (a) Slice of CNT incorporated PVA, (b) high magnification image showing aligned CNTs in PVA, (c) aligned CNT grown using CVD and (d) growth mechanism of CNT forests.	33
Figure 2.20 (a) Dry spun CNT yarn, (b) close up of yarn pulled out from free standing CNT forest, (c) SEM images highlighting super aligned nature of drawable CNT forests (scale bar: 100 μ m, inset: 200 nm) and (d) SEM of yarn; inset shows the TEM of a single thread of the yarn (scale bars: 500 nm, inset: 100 nm).....	34
Figure 2.21 (a) Schematic illustrating the presence of interconnections between CNT bundles and (b) the unzipping and strengthening of interconnections at the bottom of the forest upon drawing.....	35
Figure 2.22 Comparison of fits for hopping and tunneling conduction in CNT yarns. Better fit for the hopping model is obvious.	36
Figure 2.23 Different modes of functionalization of SWCNTs.....	37

Figure 2.24 (a) Reaction schemes for defect-site derivatization, (b) fluorination and defluorination, (c) ‘grafting to’ approach and (d) ‘grafting from’ approach of CNTs.....	38
Figure 2.25 a) Adsorption sites in CNT bundles:A-grooves of bundles, B-outer surface of sidewalls, C-interstitial cavities and D-nanotube cavities, b) cyclic molecules with varying π -electrons), c)-e) represents different adsorbed molecules on CNT surface and f) micelle formation by small molecules (top) and helical wrapping by polymers (bottom).....	40
Figure 2.26 (a) Comparison of Absorption spectra and (b) Raman spectra of pure SWNT, PmPVA and SWNT composite.	41
Figure 2.27 Structures of monomers (left) and wrapping tendency on SWCNTs (right).	43
Figure 2.28 (a) Schematic illustration of electrochromism in CNT-PDA yarns and (b) photographs of blue CNT-PDA yarn turning red under 10 mA current for 2 secs.	44
Figure 3.1 Insulating cardboard frame with window (left) and frame with CNT-PDA composite loaded and connected to an external voltage source (right).	47
Figure 3.2 CNT-PDA composite mounted on glass slide and connected to voltage source for in-situ Raman studies.	48
Figure 3.3 CNT-PDA composites oriented at 0° and 90° with respect to the laser polarization direction for polarized Raman studies.	49
Figure 3.4 Schematic of the Raman mapping process. The blue section represents the surface of CNT-PDA composite. A spot Raman spectra will be obtained from each grid and the signal intensities mapped.....	49

Figure 4.1 The various stages of CNT forest growth using thermal CVD. The times taken for each stage are shown in red.	52
Figure 4.2 (a) Drawability ranking variation of CNT forests prepared with various carbon percentages during growth and (b) ranking variations between 30 samples grown using the optimized carbon percentage (29 %).....	54
Figure 4.3 Schematic illustration of transferring CNT sheets from drawable forests on to glass slides. The magnified view of CNT alignment at various sections of the forests during the process are shown. The scale bar corresponds to 10 μ m.	55
Figure 4.4 Schematic of the CNT-PDA composites fabrication process. Monomer incorporation (left) followed by UV irradiation (right) yields CNT-PDA composites. Silver paint was used to provide electrical contacts. Current flow through CNT-PDA causes color change to red (right).	55
Figure 4.5 Evolution of crystalline PDA domains upon exposure of DA cast on silicon wafer to UV-254 nm irradiation for different times (0, 10 and 20 mins).	56
Figure 4.6 (a) XRD profiles of PDA on Silicon obtained after different UV exposure times and (b) percent conversion of DA with UV treatment time based on (200) Bragg peak.	57
Figure 5.1. (a) Schematic illustration of MWCNT-PDA fabrication and (b) the electrochromic blue to red transition.	60
Figure 5.2 (a) Digital photograph of typical device with pristine MWCNT sheets transferred to glass slide, (b) monomer incorporated MWCNT sheet, (c) partially polymerized MWCNT-PDA composite, (d) electrically induced red phase of the partially polymerized composite and (e) the blue and (f) red phase of the highly polymerized composite.	61

Figure 5.3 (a) FESEM morphology of pure MWNT sheet, (b) DA incorporated sheet, (c) partially polymerized composite, (d) partially polymerized composite after current flow, (e) highly polymerized composite and (f) highly polymerized composite after current flow. The scale bars correspond to 10 μm	62
Figure 5.4 (a) AFM surface profiles of partially polymerized blue phase (before current) and (b) red phase (after current). (c) and (d) show the profiles of blue (before current) and red phases (after current) of highly polymerized composites.	63
Figure 5.5 (a) In-situ variation in absorbance spectra with voltage of partially polymerized and (b) highly polymerized MWNT-PDA composites; (c) corresponding spectra under forward and reverse bias for partially and (d) highly polymerized composites.	65
Figure 5.6 (a) In-situ Raman spectral shifts in the region pertaining to PDA backbone of partially polymerized and (b) highly polymerized composites.....	66
Figure 5.7 (a) Raman spectra obtained at 0° and 90° configurations with respect to incident laser polarization direction for partially polymerized blue phase and (b) the corresponding electrically induced red phase, (c) intermediately polymerized blue phase and (d) corresponding electrically induced red phase, (e) highly polymerized blue phase and (f) the corresponding red phase.....	69
Figure 5.8 Raman intensity ratios ($I_{\alpha^{\circ}}/I_{0^{\circ}}$) of MWCNT-PDA composites as a function of the angle (α) between the fiber axis and the incident laser polarization axis. ..	70
Figure 5.9 (a) Proposed mechanism for electrochromism in partially polymerized and (b) highly polymerized MWCNT-PDA composites. Prior to current flow in the partially polymerized composite, short PDA backbones prefer alignment against MWCNT axis. Current flow causes realignment of PDA along the MWCNT direction. This current induced change in alignment results in de-stacking of	

PDA orbitals. De-stacking widens the bandgap of PDA, triggering the visible color change of the composites to red. Short PDA chains in the partially polymerized composites undergo realignment with little interaction with neighboring chains, eliminating stress generation; realignment of longer PDA chains in the highly polymerized composites results in physical interactions with neighboring PDA chains which hinders movement, causing a stressed structure.

.....	72
Figure 5.10 (a) The chromatic response of CNT-PDA composites to different chemicals and (b) temperature.	74
Figure 6.1 Scheme illustrating the fabrication steps for CNT-PDA composites used in this study.	77
Figure 6.2 Morphology variation as observed through optical microscope as a function of post and pre-heat treatments of PDA on MWCNT sheets. The scale bar is common for all images.....	78
Figure 6.3 (a) Field emission scanning electron micrographs of pure MWCNT sheet, (b) PDA-MWCNT prepared through route I, (c) route II and (d) route III. The scale bar corresponds to 50 μm	79
Figure 6.4 XRD patterns of composite I, II and III.	81
Figure 6.5 In-situ absorbance change with voltage for PDA-MWCNT composites prepared via routes I, II and III.	82
Figure 6.6 Critical electrochromic transition voltages for CNT-PDA composites prepared via routes I, II and III.	83
Figure 6.7 (a) Two terminal I-V plots obtained for bare CNTs, CNT-PDA, pre and post heated composites and (b) corresponding derived conductivities.	85

Figure 6.8 Evolution of $\nu_{C=C}$ of MWCNT-PDA composites prepared via route I, II and III, before, during and after the critical transition voltage.	87
Figure 6.9 (a) Raman map images for composites via route I, (b) route II and (c) route III. The horizontal scale bar corresponds to 20 μm and is common for all maps. The vertical scale bars correspond to the $\nu_{C=C}$ intensity.....	89
Figure 6.10 Calculated percentage alignment of PDA along underlying MWCNTs in composites I, II and III.....	90
Figure 6.11 (I) Proposed structures of MWCNT-PDA composites with no heat treatment, (II) post-heat treatment and (III) pre-heat treatment. UV irradiation produces a surface coating of PDA on underlying MWCNTs (I). Post-heat treatment breaks up large PDA segments and spreads them across neighboring MWCNT bundles (II). Pre-heat treatment facilitates intercalation of monomers into the gaps between MWCNT bundles, resulting in high π -stacking interactions at the MWCNT-PDA interface after UV irradiation (III).	92
Figure 7.1 Steps involved in the fabrication of CNT-ZnO-PDA hybrids.....	95
Figure 7.2 Photographs of CNT-ZnO-PDA hybrids with increasing loading of ZnO. 96	
Figure 7.3 FESEM micrographs of (a) MWCNT bundles and (b) CNT-ZnO-PDA hybrids with 5 % ZnO loading. The scale bar corresponds to 50 μm	97
Figure 7.4 (a) Xray Diffractogram of ZnO nanoparticles incorporated in the hybrids used in this work and (b) typical transmission electron microscope image of ZnO np's, confirming the average particle size ~ 100 nm.	98
Figure 7.5 (a) Tracking of main peak absorbances for the blue and red phase of CNT-ZnO-PDA hybrid and (b) estimating the reversibility of the transition in the hybrid at critical transition voltage of 7 V.	99

Figure 7.6 In-situ Raman point spectra for the hybrid based on $\nu_{C=C}$ obtained before, during and after application of critical transition voltage of 7 V.....	100
Figure 7.7 (a) Raman map before and (b) after current flow in CNT-PDA and (c) the corresponding Raman map before and (d) after current flow in CNT-ZnO-PDA hybrid. The horizontal scale bar corresponds to 20 μm . The vertical scale bar corresponds to Raman intensity (0 as black and 3k as white).	102
Figure 7.8 (a) Two terminal I-V plots obtained for bare CNT sheet, CNT-PDA and CNT-ZnO-PDA and (b) the corresponding derived conductivity values.	103
Figure 7.9 (a) XPS survey scan of CNT-ZnO-PDA hybrid before current flow and (b) after current flow. The insets show the Zn $2p_{3/2}$ peaks corresponding to ZnO.	104
Figure 7.10 Comparison of the absorbance peak shifts in the blue phase of conventional CNT-PDA and CNT-ZnO-PDA hybrids.	106

List of Tables

Table 4.1	Ranking criteria for CNT forests grown towards this research.....	52
Table 4.2	The optimized growth parameters for drawable CNT forests.....	53
Table 6.1	Heat treatment processes for composites I, II and III.....	77
Table 6.2	Comparison of the Raman shifts and intensities before during and after application of critical transition voltage in composites made through routes I, II and III.....	88
Table 7.1	Comparison of Raman shift and intensity variations before, during and after applying critical transition voltage in CNT-ZnO-PDA composites.....	101

Abstract

Materials that have the inherent ability to respond to external stimuli with a visible color change have tremendous potential in the field of sensing. It is unlikely that a single material exhibits all the favorable properties required for use of such chromatic systems practically. For instance polydiacetylenes (PDA) have the inherent ability to change color in response to external stimuli, however, the physical attributes of these polymers are poor. By combining the useful stimuli response of PDAs with physically robust materials, composites with the positive attributes of both can be obtained. A literature study conducted towards this end has revealed that carbon nanotube (CNT) fibers are ideal for forming composites with PDAs not only because of the improved mechanical properties of the resulting composite, but also because it invokes an electrically induced chromatic transition of the same.

Although the phenomenon of electrochromism in CNT-PDA composite fibers has been observed, an understanding of the influence of CNTs on the color transition is limited. This work explores the science behind electrochromism in CNT-PDA composites, by systematically studying composites prepared through different strategies. This research provides insight into the science of electrochromic CNT-PDA composites and facilitate tailoring the properties of these composites to provide some degree of control over the electrochromic transition.

Towards achieving the objectives of this research, CNT-PDA composites with different extent of polymerization were prepared. To understand the effect of order in the PDA layers on the electrochromism, the composites were exposed to different types of heat treatments. Further, ZnO nanoparticles were used as an anchoring phase to prepare unique CNT-ZnO-PDA hybrids. The electrochromism in these composites was explored in detail using in-situ spectroscopy and surface characterization tools.

Although both partially and highly polymerized CNT-PDA composites exhibited electrochromism, it was found that the electrically induced red phase in CNT-PDA composites need not have stressed PDA backbones, unlike other forms of PDA chromism induced by heat and solvents. It was also found that heat treatment in general, increased the critical electrochromic transition voltage in CNT-PDA composites. Specifically, heat treatment before polymerization increased the chromatic contrast and critical transition voltage significantly when compared with conventional CNT-PDA composites. In contrast, incorporation of ZnO to form CNT-ZnO-PDA hybrids lowered the critical transition voltage but significantly improved the recovery of blue phase when electric stimulus was removed. Detailed mechanistic interpretations of the structural changes responsible for the different electrochromic behaviors in these composites are provided in this thesis.

Chapter 1 Introduction

1.1 Background and motivation

Of the five primary senses of the human body, the sense of vision is the most developed. Consequently, changes in the color emitted by an object can be naturally detected by humans, without the use of sophisticated and expensive instruments. This simple and apparently straightforward principle is the driving force behind research on the design of chromatic material that can reversibly change color in response to different stimuli. Numerous reports of chromatic changes in materials induced by stimuli such as temperature, pH and light are available in the literature. However, for practical applications in sensing, electrical stimulus is most useful.

Composite capable of electrically induced and reversible color change has potential applications in the in-situ, non-destructive testing of structural integrity of components. Traditional non-destructive detection of defects usually involves dismantling of the component, which inevitably causes degradation. Composite chromatic yarns/fibers incorporated into structural components can confirm the absence of defects by changing color in response to the current passed through the fiber. Being light-weight, flexible and weavable, such systems will also have commercial and military applications, where ‘smart’ uniforms can be finally realized by weaving fabrics out of the composite fibers.

Conjugated polymer systems like polydiacetylenes (PDA) appear to be the ideal candidates to develop tunable chromatic characteristics as they combine good conductivities with processability and flexibility. Blue PDAs have been known to switch to a red state on exposure to certain stimuli such as pH and temperature. Reversibility of the colored state on removal of stimuli however, is not guaranteed. The range of

effective stimuli is also narrow, limiting practical applications of these polymers in sensing.

Investigations on the structure-property relations of various polydiacetylenes have revealed links between conformation of the polymer backbone and delocalization of π -electrons on the color exhibited. It is believed that reversible color changes in such conjugated polymers can be achieved by controlling the chain conformation and nature of electron delocalization along the polymer chain. One possible route to achieve control over the chain conformation and electron delocalization of PDAs is by incorporating carbon nanotubes (CNTs). The presence of delocalized π -electrons as well as the effect of curved surface of CNTs can influence the electron delocalization and chain conformation of PDA, thereby inducing chromatic change.

In the only reported work of electrochromism in PDAs induced by current flowing through CNT fiber, the diacetylene precursors were attached on the CNT fiber surface by very weak, non-covalent forces. The color change of the composite fibers on passing current was attributed to disordering of PDA under the electric field generated by CNTs, similar to intrinsic chromism mechanisms of PDA to other stimuli such as heat, pH and light. However, it should be noted that chromism mechanisms in PDA were established through in-situ spectroscopic studies on PDA systems in solution, where the polymer side chains have a higher degree of freedom, which is in stark contrast to the case of solid state CNT-PDA fibers and yarns. Moreover, there are reports where the red phase of certain PDAs have an even more ordered structure than the corresponding blue phase, implying that disordering of PDA is not the only cause for chromism in PDA. Thus, investigating the dynamics of CNT-PDA electrochromism through in-situ spectroscopy techniques modified to suit composite fibers rather than PDA in solution will potentially reveal a new mechanism for electrochromism in CNT-

PDA, unlike those previously established for intrinsic chromism PDAs in solution. Further, as chromism of PDA can be influenced through heating and metal oxide anchoring, their effects on the electrochromism of CNT-PDA hybrids is of interest for developing voltage specific and reversibly electrochromic hybrids.

1.2 Objectives

- 1) The primary objective of this work is to realize electrochromism in CNT-PDA composites and validate the existing hypothesis which attributes polarization of bulky side groups of PDAs as the cause of color change.
- 2) The second objective is to alter the critical transition voltage (V_C) of CNT-PDA through post and pre-polymerization heat treatment processes to fabricate composites that switch from blue to red at specific voltages.
- 3) As long term reversibility of the electrochromic transition in CNT-PDA is poor, the third and final objective of this work is to improve reversibility of the transition through surface anchoring of PDA onto Zinc Oxide nanoparticles.

1.3 Scope

- 1) Review of the synthesis of vertically aligned CNT forests, macroscopic CNT assemblies and its chemistry to understand the influence of CNTs on the properties of CNT-PDA composites.
- 2) Review of the science behind chromatic transitions in different forms of PDAs.
- 3) In-situ studies before, during and after current flow to understand dynamics of the blue to red transition in CNT-PDA.
- 4) Investigate effects of heat treatments on the critical transition current in electrochromic CNT-PDA composites.

- 5) Validate the effect of Zinc Oxide anchoring on the reversibility of electrochromic transition in CNT-ZnO-PDA composites.

1.4 Outline of the thesis

This thesis is organized into 8 chapters. Chapters 1 and 2 introduce the reader to the objectives and scope of the research work undertaken and detailed background information supported by relevant literature. The different steps involved in sample preparation and all of the experimental techniques used towards this research work are explained in Chapter 3. Chapters 4-7 provide in depth investigations, including experimental procedures, data analysis, and discussions aimed towards achieving the objectives of this research. In Chapter 8, the key conclusions drawn from the investigations carried out are summarized along with suggestions for future work.

Chapter 2 Literature review

2.1 Chromism

Although most of us take it for granted, color plays an extremely important role in our daily lives. Ever since the relationship between light and color was recognized by Newton in the late seventeenth century, the understanding of the science behind color has been progressing gradually [1]. Chromism is a process that induces change in the colors of compounds. In many cases the change is reversible and induced by changes in electronic states of molecules. Hence, external stimuli which can alter the electronic state of molecules can induce color changes within the material.

2.2 Types of chromism

Changes in the electronic states, namely π and d-electron states trigger color changes within the material. When the cause of this change in electronic state is an external stimulus, and the induced change is reversible, the potential applications of the material increase. Figure 2.1 shows the five major classifications of chromic material based on the type of stimulus inducing the change in each case. Apart from the materials with intrinsic chromism, synthetic materials with desired chromic effects have been synthesized to respond to a wide range of stimuli over the past two decades. A detailed study of all the chromic systems is beyond the scope of this thesis. However, a brief summary of the scope and developments of the five main classes of chromism are provided.

Thermochromism was defined as an easily noticeable reversible color change brought about by the melting point for solids or the boiling point of the solvent in case of a solution, by Day et.al [2]. Based on whether heat is the sole cause or if the changes in environment brought about by heat causes thermochromism, materials exhibiting

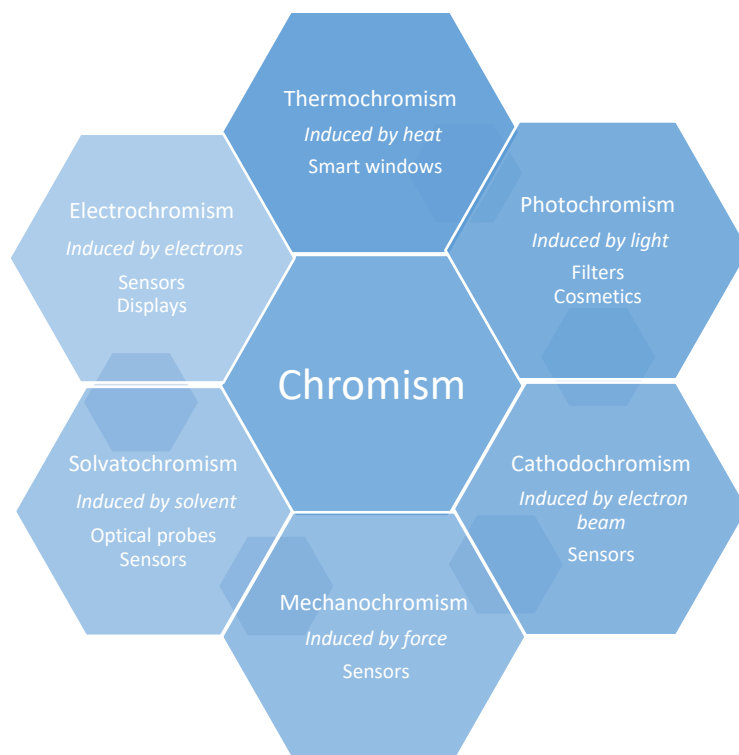


Figure 2.1 Classification of types of chromism.

thermochromism are classified as ‘intrinsic’ and ‘indirect’ systems, respectively. Thermochromic windows are based on intrinsic systems while reversible indirect thermochromic materials find use as organic pigments [1]. Intrinsically thermochromic conjugated polymers are also used in optical temperature indicators [3].

When a compound undergoes a reversible change between two states having separate absorption spectra on exposure to light, the phenomenon is called photochromism. Usually, the change is initiated by UV light. The visible color change of such material are accompanied with corresponding changes in refractive index, dielectric constants, redox potentials as well as geometrical structure. These factors facilitate the use of photochromic materials in numerous fields such as cosmetics, heat measurement, optical memories for data storage, photo-optical switches, filters, displays and self-developing photography to name a few [4].

If materials exhibit changes in either absorption or emission spectra when dissolved in different solvents, the phenomenon is referred to as solvatochromism [1]. If the interaction with solvent results in changes in only the emission spectrum, it is called solvatofluorochromism and is associated with transition metal carbonyl complexes. Initially, solvatochromism was used to characterize solvents or to understand excitation behavior of chromogenic solutes [5]. In the past two decades, solvatochromism has been employed extensively in the field of optical probes and sensors.

Materials which have the ability to persistently and reversibly switch between color states as a result of a redox reaction initiated by an applied electric field is considered to be 'electrochromic' and the phenomenon is referred to as 'electrochromism'[6]. The most commonly studied electrochromic materials included transition metal oxides like tungsten oxide (WO_3), organic viologens, inorganic complexes, namely Prussian Blue (PB) and conjugated/conducting polymers [7].

Apart from the traditional redox reaction initiated electrochromism, conjugated polymers are capable of structural changes in response to external stimulus, such as electric current, which yields a different colored state. Restoration of the original polymer chain structure when the stimulus is removed will yield a reversible color change. This direct link between structure and color which can be controlled by an external stimulus is an appealing prospect in the field of sensing devices. This combined with the improved processability, faster switching and color tunability as opposed to their inorganic and molecular counterparts make them very attractive. As the conducting polymer polydiacetylene (PDA) is the chromatic material of interest in this work, the following sections (2.3 and 2.4) are devoted to understanding the origin of color and stimuli induced color changes in PDAs.

2.3 Basics of polydiacetylenes

PDA being a conjugated polymer (CP) essentially comprises of a combination of unsaturated linkages and/or aromatic ring systems and sometimes conjugating heteroatoms. Conducting polymers exhibit changes in their absorption, emission and redox properties as functions of various forms of external stimuli [8]. The combination of back bone conjugation with specific properties of these polymers such as high flexibility, high impact resistance and low density, makes them very attractive and it is not surprising that lot of work has been carried out on the development of CPs.

It is widely accepted that CPs exhibit semiconducting behavior and consequently, their photo absorbance and emission properties can be described by band-gap theory. In the case of trans-polyacetylene, which is a typical CP, each carbon is sp^2 hybridized. This means that the polymer can be considered as a one dimensional analogue of graphite with the primary difference between the two being the C-C bond lengths; while the C-C bond lengths are equivalent in graphite, in the polyacetylene back bone, the C-C bonds are alternatively slightly longer and shorter, owing to Peierls distortion (Figure 2-2a and b). It is this bond non-equivalence in the back bone that opens up a gap between the HOMO level of the valence band (π band) and the LUMO level corresponding to the conduction band (π^* band). It so happens that the band gap in most PDAs facilitate absorption of energies in the red region of the visible spectrum, causing a $\pi \rightarrow \pi^*$ optical transition, making the polymer appear blue to us (Figure 2.2c).

In addition to being strongly colored, PDAs possess certain unique structural and electronic properties which trigger changes in optical characteristics of the polymer in response to variations in the polymer environment caused by stimuli such as temperature, pH etc [9, 10]. Though typically produced as aqueous suspensions or thin films on solid substrates, the easy immobilization of PDA on diverse surfaces have

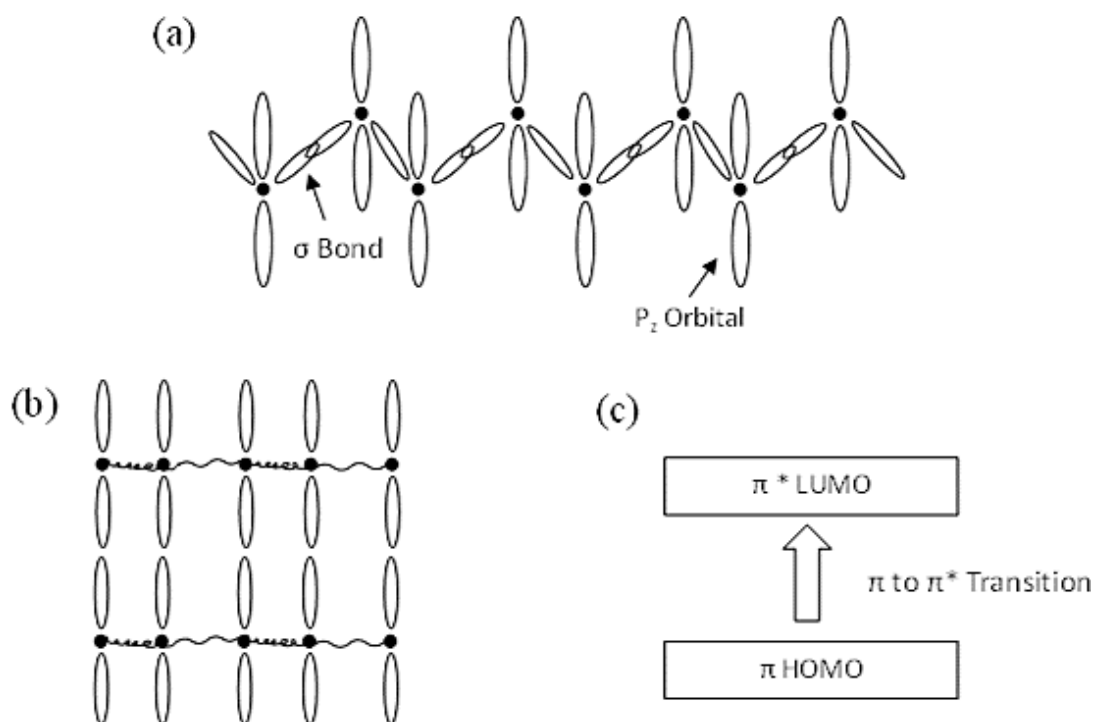


Figure 2.2 a) Schematic representation of σ -bonds and p_z orbitals in polydienes, b) Peierls distortion in polyacetylene and c) HOMO-LUMO transitions [1].

recently resulted in PDA microarray sensors, micro fluidic devices and PDA embedded electrospun microfiber sensors as illustrated in Figure 2.3 [11].

The absorption characteristics of PDA depends on the structure of the polymer side chains, extent of polymerization, the form of the final polymer and the environment of the polymer [11]. Hence, there is scope to tailor the properties of the PDA to make it responsive to other forms of stimuli, including but not limited to, electric current. With the realization that PDAs can be easily formed as self-assembled systems, significant effort was put into understanding the origin of chromic changes in different forms of PDAs. The science behind polymerization of diacetylene monomers and the resulting chromic changes exhibited by PDAs on exposure to stimuli is discussed next.

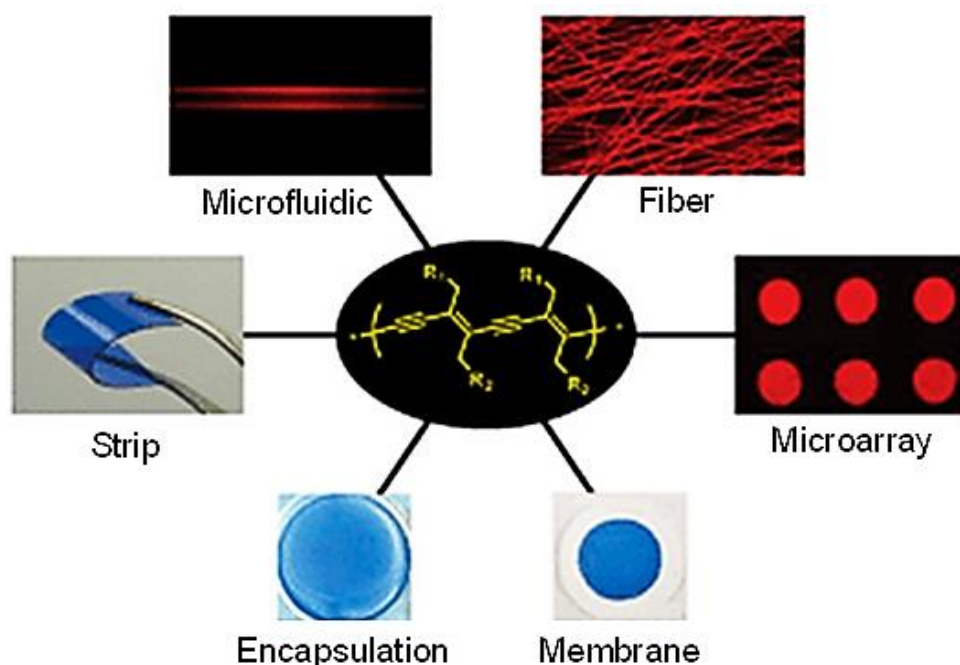


Figure 2.3 Recent conceptually new developments in PDA applications [11].

The diacetylenic precursor typically consists of a polar head and a hydrophobic tail (Figure 2.4a). The tail can be further divided into three portions comprising the alkyl spacers between the head group and diacetylene moiety as well as the terminal alkyl chain. 1,4-polymerization of conjugated dienes in solution has been achieved rather easily with the use of simple catalysts. Although diacetylenes share a similar conjugated structure to dienes, polymerization of diacetylenes proved to be extremely difficult.

In 1969, Wegner et al. [12] successfully carried out the solid-state 1-4-addition polymerization of diacetylene monomers. The polymerization proceeded via a topochemical mechanism under UV light or thermal initiation and required reactive monomers to be preorganized at a distance commensurate with the repeat distance in the final polymer (Figure 2.4b). Understandably, the stringent requirement on monomer preorganization made the polymerization process unreliable.

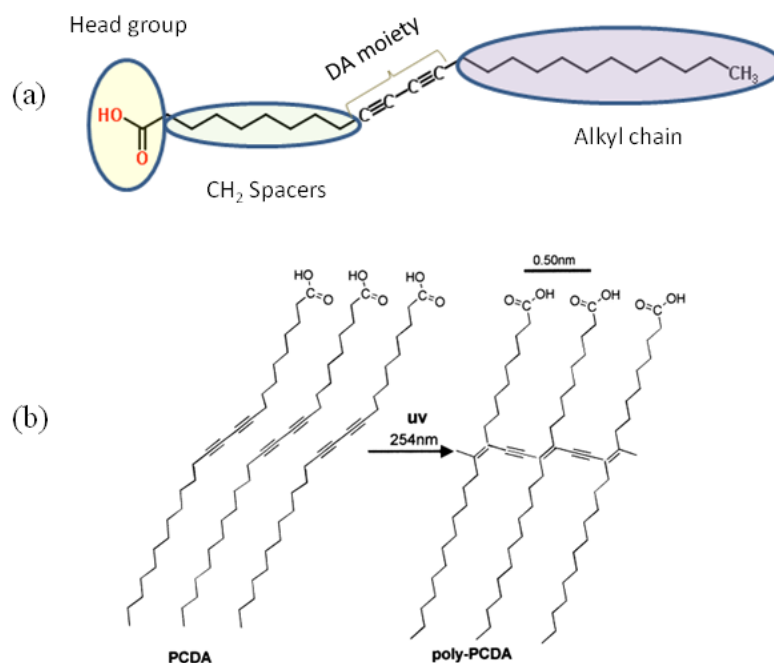


Figure 2.4 (a) General structure of diacetylene precursor and (b) topochemical polymerization process of PDA [12].

An alternative strategy to synthesize PDAs using a supramolecular host-guest strategy was proposed by Fowler et al. [13]. The method utilizes a host material which imposes necessary structural parameters on diacetylene monomers that under normal circumstances will not polymerize. With the strict adherence of preorganization of monomers no longer a requirement, this method was successfully used to synthesize a great variety of diacetylenes and other reactive monomers.

2.4 PDA Chromism

Detailed investigations of the special properties of PDAs were made possible when Patel et al. [14] discovered that adequate choice of side-groups can facilitate dissolution of PDAs in common organic solvents like CHCl₃, DMF, Nitrobenzene and THF. Typically, diacetylene monomers are colorless while the polymerized form exhibits a blue color. Due to the inherent special structural and electronic features of the polymerized form, external stimuli cause a dramatic color shift to red, evidenced by the

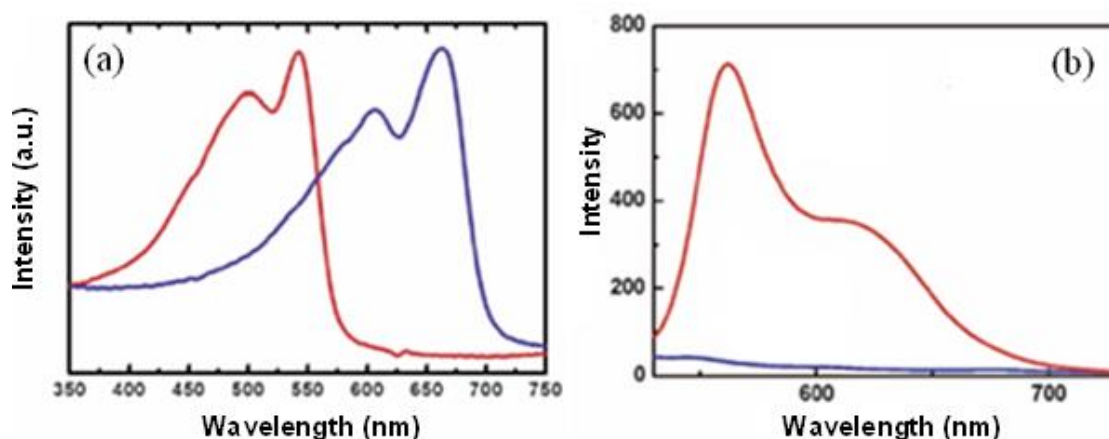


Figure 2.5 (a) Typical visible spectra of blue and red phases of PDA and (b) Fluorescence spectra [10].

shift in absorption peaks before and after subjection to stimuli (Figure 2-5a). Further, fluorescence spectroscopy studies revealed that the red state of PDA was fluorescent (Figure 2.5b). The dramatic color change in PDA solutions from yellow to red or blue in response to changes in temperature and solvent/non-solvent ratio, sparked the interest of several research groups [15-18].

Most of the early work on PDAs was carried out using the polymers P4BCMU, P3BCMU and PTS12. Two structural models were proposed to explain the color transitions occurring in these PDAs. The first suggested an intra-chain coil to rod conformation change as the factor responsible for color change [16, 17]. The second model referred to as the fringed micelles model, attributed the transition to the aggregation of semi rigid chains into clusters [17-19]. Experimental evidence gathered over the years seems to favor the latter aggregation model. A brief overview of the critical results leading to the acceptance of the aggregation model over the intra-chain coil to rod transition is provided in this section.

In the early 80's, Patel et al. [20] attributed the color change in PDA solutions to a single chain planar-non planar conformational transition with a strong coupling of the delocalized π electrons to the polymer conformation. As only the backbone is

conjugated, the visible optical absorption in PDAs can be seen as an indication of the backbone structure. Hence, broadening and shifting of the absorption peaks are evidences for chain conformational change for substituted PDAs in general. Infrared spectroscopy studies have confirmed that H-bonding between NH groups induce a spectral shift of about 100 cm^{-1} and a large increase of the absorption intensity in the red phase [21]. Subsequently, these results were used by Patel et al. [20] to support the claim of a planar-non planar conformation change at color transition. However, opinions differed due to the fact that spectroscopy could not prove the absence of aggregation.

Field induced birefringence experiments were carried out to relate the observed birefringence to chain conformation. The study was based on the fact that light intensity detected due to field induced orientation is proportional to $(\Delta n)^2$, where Δn is the birefringence. Even though the ratio of $\Delta n(\text{rod})/\Delta n(\text{coil})$ was found to be greater than 300 by Lim et al. [22], the result could not be considered as concrete proof for rod-like chain structure of the PDAs. This is because the study could not confirm whether the change in birefringence was induced by orientation of rod-like molecules or large aggregates in which the individual chains are more or less aligned [23]. Quasi elastic light scattering experiments were also not convincing and in fact, no robust experimental results exist to prove the existence of rod conformation in solution.

In an attempt to verify the formation of aggregate structures, Wenz et al. [18] performed light scattering experiments on P3BCMU dissolved in 1,2-dichloroethane. MW was calculated as 2×10^8 , which when compared to the MW of the macromolecule, suggests the existence of an aggregate structure with 150-200 chains. Muller et al. [19] performed similar scattering experiments on P4BCMU dissolved in toluene at 20°C with $\text{MW} = 1.67 \times 10^6$ and $\text{MW}/\text{MN}=2.5$. Comparison with MW of isolated macromolecules again suggested an aggregate structure. Objections were raised regarding

conclusiveness of the results in both cases as the large increase in intensity could be brought about by change of the refractive index.

In order to obtain absolute measurements, SANS experiments were carried out by Wegner et al. [24]. P3BCMU and P4BCMU samples with comparatively low MW (~ 43200) and reasonable polydispersity were used in the study. The scattering functions measured in the yellow and red phases showed a large increase of intensity, confirming the occurrence of an aggregation process. However, it should be noted that the physical origin of the color transition was still unclear and it was not possible to rule out an aggregation process triggered by a single chain phenomenon.

2.5 Significance of PDA backbone fluctuations

Raman studies on CP solutions suggested the electronic wave functions had localized to a distribution of short ‘conjugation lengths’, which is a parameter describing π -electron delocalization along the backbone [21]. In good solvents, CPs are semi rigid and the effect was attributed to the influence of conjugation at a local scale [14, 17]. The conjugation length is proportional to the average overlap of π orbital, which in turn corresponds to the geometry of the molecule. Curvature and torsional fluctuations of the backbone influences the geometry of the macromolecule. The change in geometry invariably decreases conjugation length and hence a direct link between chain conformation and electronic properties is obvious [25-27].

As already mentioned, pure PDAs are insoluble in most solvents, and hence, to make PDAs soluble, one has to resort to various pendant groups. The side groups are usually very long and can be considered as short chains, with up to 90% of the atoms of the monomer unit belonging to the side groups. Hence, it is expected that the side groups exhibit a significant influence on the chain conformation in PDAs. Apart from the

pendant side groups, delocalized π -electrons and the nature of head groups will affect the chain conformation. The following sub-sections discuss these parameters in detail.

2.5.1 Influence of side groups

Wenz and Wegner et al. [18, 28] proposed a worm like chain model leading to a ribbon like structure for PDAs. They studied the correlation within the chain by measuring the average size of the coil as a function of the molecular weight and observed a dependence of the radius of gyration on the molecular weight:

$$\langle R_G^2 \rangle_z = 0.45 M_W^{0.55} \quad 2.1$$

The radius of gyration for an equivalent perfect random coil is given by:

$$R_{GC}^2 = N_W a^2 / 6 \quad 2.2$$

Where $N_W = M_W/m$, the number of monomer units for a chain with mass M_W and 'a' is the monomer unit length. Figure 2.6a shows the variation of characteristic ratio ($C_p = \langle R_G^2 \rangle_z / R_{GC}^2$) as a function of degree of polymerization (P_w). It was observed that the C_p of the worm like chain increased initially and reached a plateau value. When the chain length increased, the C_p limiting values also increased.

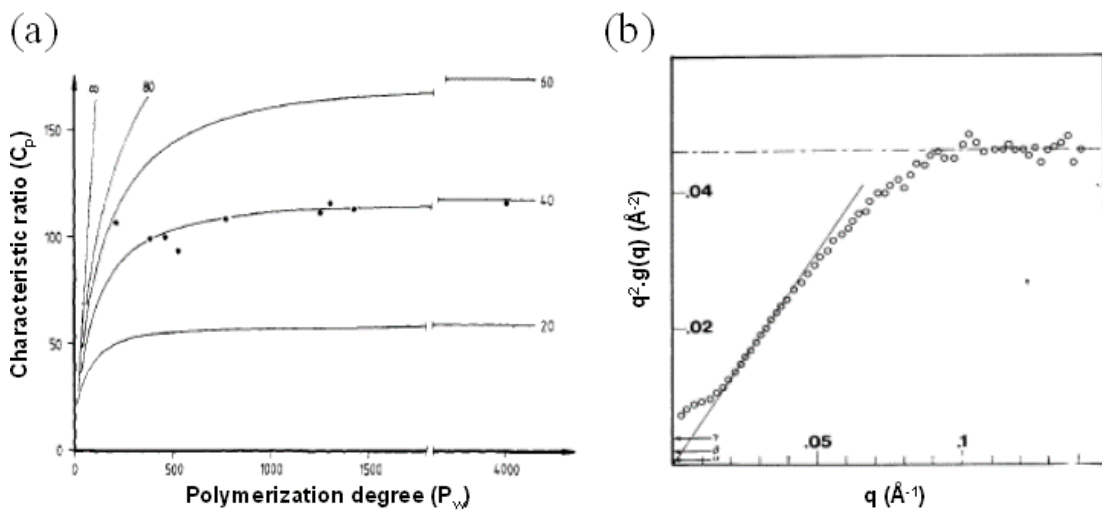


Figure 2.6 (a) Characteristic ratio (C_p) vs degree of polymerization (P_w) and (b) $q^2 g(q)$ versus q plot of P3BCMU in DMF [18].

The initial linear increase in C_p corresponds to the behavior of a stiff rod while the flat plateau region describes that of a random coil. The result clearly indicates that even very stiff chains exhibit random coil like behavior if the length is long enough. Using the same approach of comparing C_p for P3BCMU and PTS12, the authors wrongly concluded that side groups have no or little influence on the chain conformation.

The worm-like chain model was validated by analyzing the plot of $q^2g(q)$ versus q (Figure 2.6b), where:

$$q = \frac{4\pi}{\lambda} \sin \frac{\theta}{2} \quad 2.3$$

And

$$g(q) = \frac{M_w}{m} P(q) \quad 2.4$$

The model determines the point at which the curve crosses the $q^2g(q)$ axis; α corresponds to the worm-like chain model while β and γ represent the rigid model. As only α fits the experimental data well, it was accepted that the worm-like model is the best approximation for PDAs.

Bargain et al. [29] could not explain the results obtained for SANS experiments with PTS12 dissolved in DMF and nitrobenzene based on a worm-like chain model. They observed that the chain statistics were well described by the worm model but the thermal behavior was not as predicted. Bredas et al. [30] attempted to understand the reason behind the unpredictable behavior and a brief outline of the resulting work is described below.

In the worm-chain model, the polymer chain is defined as an infinitely thin thread (Figure 2.7a). It stands to reason that the contradiction arose due to some difference in the real scenario. An alternative structure for the polymer with the

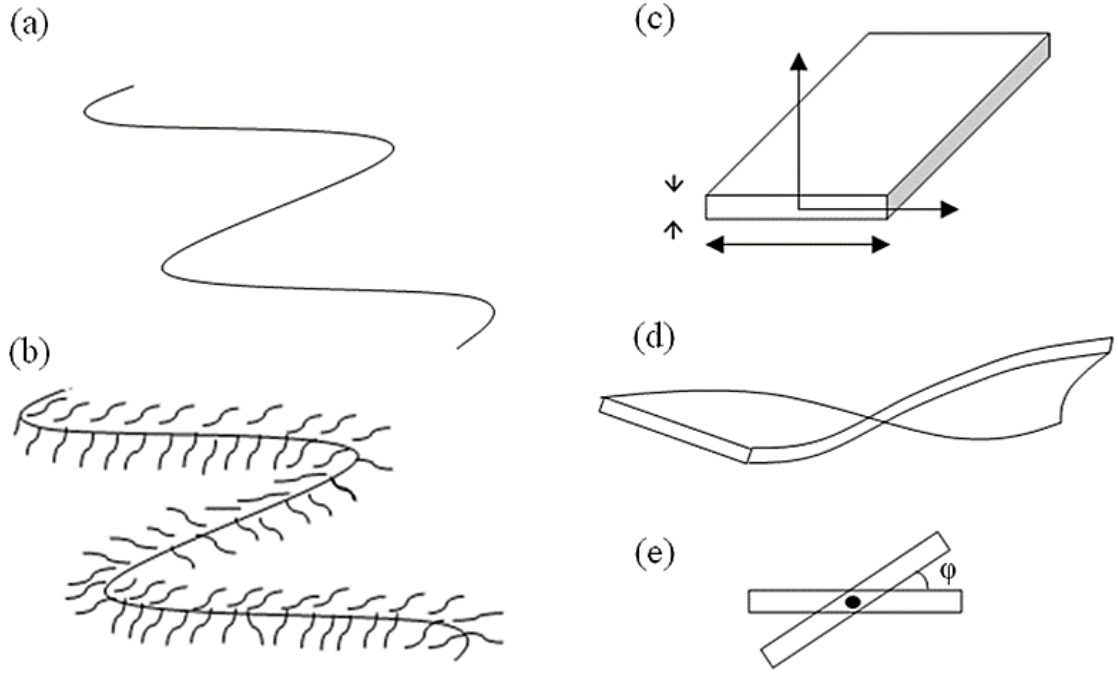


Figure 2.7 (a) and (b) shows polymer chains with and without side groups respectively; (c), (d) and (e) correspond to model for ribbon-like structure with continuous angular deviation [23, 30].

backbone and lateral parts of the monomer forming a homogeneous unit with simple geometrical forms was considered by Bredas et al. [23, 30] (Figure 2.7b). The extension of the side group into the solvent is the unique parameter in this case. Assuming rectangular cross-sections, two additional lengths were defined for the polymer chain as indicated in Figure 2.7c.

The local curvature of the polymer chain with lateral side groups is obtained using a quadratic expression [30]:

$$\Delta F = \frac{1}{2} \int_L EI \left(\frac{d\theta(l)}{dl} \right)^2 dl, \quad (2.5)$$

where E is the elastic modulus, I the moment of inertia and $\theta(l)$ is the angle between unit vectors at two points separated by distance l in backbone. For the lateral extensions of the backbone, the average effective moment of inertia is obtained as:

$$\langle I_e \rangle = \frac{1}{\Phi} I_1 \int_0^\Phi \sqrt{1 - k^2 \cos^2(\beta)} d\beta \quad (2.6)$$

Where $k^2 = 1 - (I_2/I_1)^2$ and β is the angle between bending plane and principle bending plane. The two limiting cases are defined by $\Phi = 0$ (planar ribbon structure) and $\Phi = 90$ where Φ is the angle of rotation between neighboring monomers (Figure 2.7e). The statistical length of the polymer chain with lateral groups is obtained as:

$$b = \frac{2E \langle I_e \rangle}{T} \quad (2.7)$$

From above equation, it follows that neighboring side groups repel each other, causing straightening of the side groups. Moreover, packing along the backbone induces a torsional force between side groups, promoting a non-planar structure (Figure 2.7d). It was deduced that the increase of angular deviation between adjacent monomers in the PDA requires very little energy, of the order of $0.6 \text{ kcal mole}^{-1}$ [30]. Hence, heating the PDA provides more than the required energy to increase torsional fluctuations to alter local conformation or rigidity of the macromolecules.

2.5.2 Influence of π -electrons

In general, experimental measurements suggest that the chain conformation and π -electron delocalization in the backbone of PDAs are linked. A detailed theoretical study was carried out by Schweizer et al. [31] to understand the role played by π -electron delocalization on the solvation effect of CPs. I.G. Kaplan determined that in the case of saturated polymers where only σ -bonds are involved, the attractive interaction between two chains containing N units and intermolecular separation of R , is proportional to N^2/R^6 [32]. For conjugated polymers, the spatial extension of the π -electron system is expected to lead to a different attractive interaction between chains. Subsequently, Schweizer et al. [31] obtained the interaction between conjugated macromolecules and the solvent units as a function of the electron delocalization as:

$$\begin{aligned}
\langle \Delta V \rangle &= -C_\lambda \sum_{N_S} \sum_{\xi_\lambda} \frac{3}{2} \frac{\Delta \alpha_p(\lambda)}{\xi_\lambda} \pi r^2; C_\lambda \\
&= \frac{I_S I_\lambda}{I_S + I_\lambda} \rho_S \alpha_S \langle R^{-6} \rangle_\lambda
\end{aligned} \tag{2.8}$$

where, I_S and I_λ are the ionization potentials of the solvent unit and submolecule λ respectively, ξ_λ is the conjugation length and $\Delta \alpha_p(\lambda)$ is the varying part of the polarizability depending on the size of the submolecule. However, it should be noted the model excluded any monomer-monomer interaction [23]. The Schweizer model predicts an increase in rod conformation of the CP as a result of attractive polymer solvent interaction.

For conjugated molecules involved in CPs, the total interaction energy includes contributions from both σ as well as π electrons and can be expressed as follows:

$$E_{int} = E_{\pi\pi} + E_{\pi\sigma} + E_{\sigma\sigma} \tag{2.9}$$

Obviously, the term $E_{\sigma\sigma}$ occurs usually for saturated polymers. The interaction term $E_{\pi\pi}$ results from either polymer-polymer or polymer-solvent interactions and is dependent on the effective conjugation length. Kaplan I.G. [32] obtained the following qualitative relationships for polyenes with $R \gg L$:

$$E_{\pi\pi} \propto \frac{L^5}{R^6}, \quad E_{\pi\sigma} \propto \frac{L^3}{R^6}, \quad E_{\sigma\sigma} \propto \frac{L^2}{R^6} \tag{2.10}$$

Hence it was suggested that the $E_{\pi\pi}$ interaction appears strongest. As early as 1955, it was observed by Haugh et al. [33] that the contribution of $E_{\pi\pi}$ interaction becomes dominant with increase in conjugation length. Taking these facts in perspective, Bredas et al. [23] suggested that when $E_{\pi\pi}$ becomes dominant, the macromolecule folds with an attractive interaction (Figure 2.8). When the concentration is large, even bundles and fringed micelle structures may be formed.

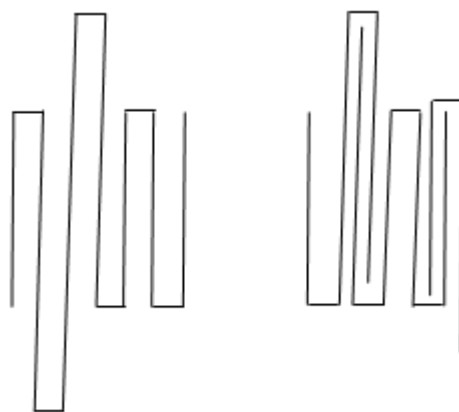


Figure 2.8 Chain folding at low concentration (left) and high concentration (right) of π -electrons.

2.5.3 Influence of head group

To correlate the nature of the head group with chain conformation and chromatic transitions, PDA vesicles synthesized from three monomers, 10,12-tricosadiynoic acid (TCDA), 10,12-pentacosadiynoic acid (PCDA) and N-(2-aminoethyl)pentacosadiynoic acid (AEPCDA) were studied and interesting conclusions were made [34].

Thermal energy improves dynamics of all segments of PDA such as alkyl tails, diacetylene moieties and polar heads. Color transition occurs when the thermally induced motion overcomes all other inter and intra-chain interactions within PDA, resulting in significant rearrangement and release of strain in the backbone [11, 35]. It has been suggested that when the perturbation induced is small, the color change is reversible.

The absorption spectra at room temperature exhibits similar pattern for polymers prepared from the three different monomers. Increasing temperature caused the spectra to shift to high energy region and showed a decrease in absorption in the case of PTCDA and PPCDA. A plot of λ_{max} against temperature indicated a higher magnitude of segmental rearrangement in PTCDA and it was attributed to the smaller inter and intra-chain dispersion due to shorter alkyl chain and lack of H-bonds. In the case of

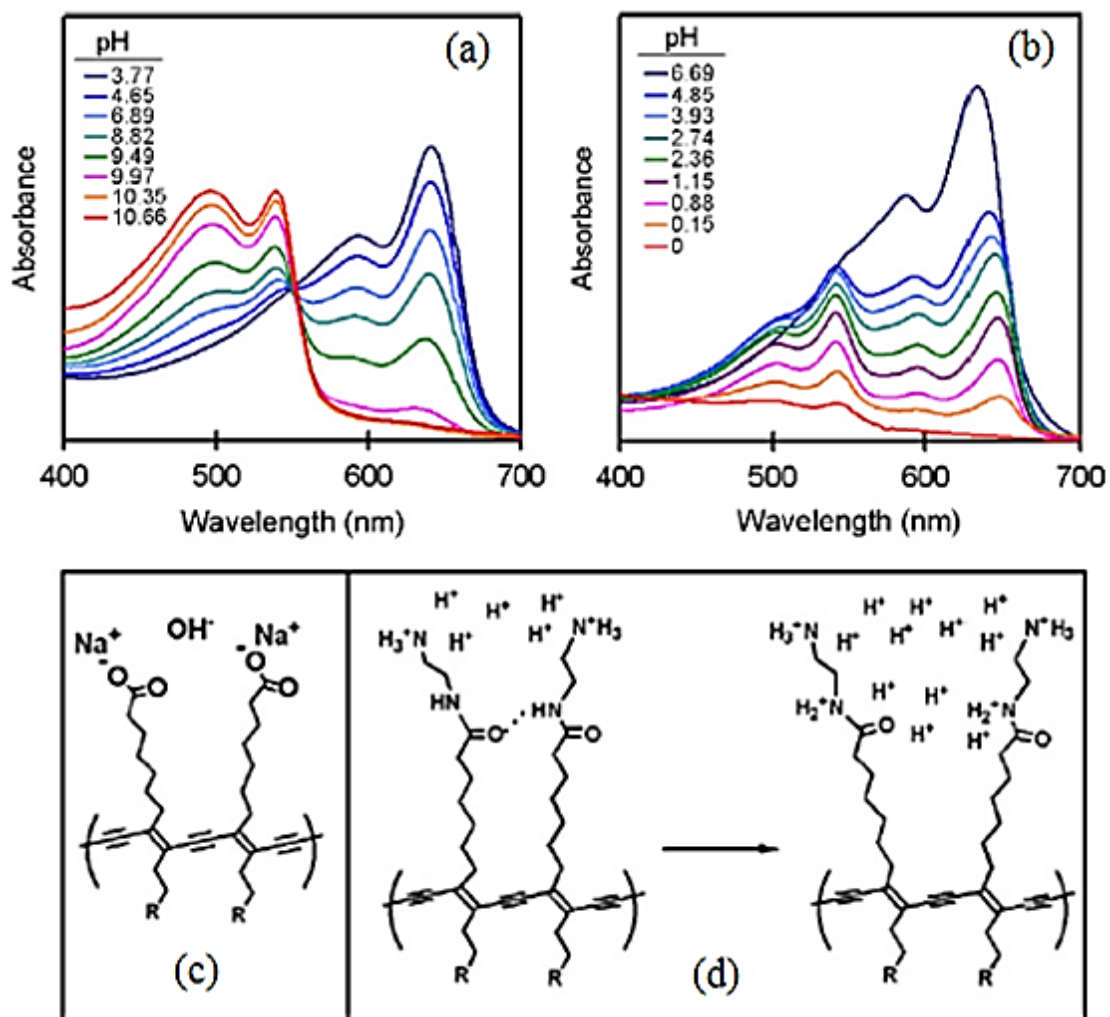


Figure 2.9 (a) Absorption spectrum of PPCDA and (b) PAEPCDA in response to change in pH; (c) PPCDA in high pH region and (d) PAEPCDA in low pH region [34, 36].

PAEPCDA, the color transition occurred about 15°C lower than the other cases. As PPCDA and PAEPCDA had identical tails and differed only in the head groups, a logical interpretation of the absorption spectrum of PAEPCDA linked the discrepancy to the H-bonds between head groups.

The introduction of OH⁻ ions removes acidic protons from the carboxylic heads, causing breakage of H-bonds [36]. It also converts the carboxylic group into carboxylate, making it negatively charged. The key result is that the head groups become mutually repulsive in a pH environment, causing rearrangement of PDA segments. The

number of carboxylic groups determines the magnitude of segmental rearrangement [34].

The absorption spectra obtained on increasing pH from 4 to 8.8 are shown in Figure 2.9a. The systematic growth of peak at 540 nm corresponds to the increase in negatively charged carboxylate groups. Increasing pH to 10 causes an abrupt change in the spectra corresponding to a complete transition. Similar spectral features are observed for PTCDA and PPCDA although the transition occurs at a lower pH for the former, owing to the weaker ionic repulsive force required to induce color change in PTCDA.

As observed from Figure 2.9b, the absorption spectrum of PAEPCDA is different as it requires addition of H^+ ions to initiate color transition. The outermost layer of PAEPCDA comprises of amine groups with H-bonds. Unlike previous cases, OH^- ions cannot abstract protons from amine groups. H^+ ions when introduced, protonate the N atom in amine group. Repulsive ionic interaction induces slight color change, with similar interactions of H^+ with N atoms of amide groups and ethyl groups, resulting in complete color transition at 0 pH. The difference in mechanism in both the cases is highlighted in Figure 2.9c and d.

These results indicate that the nature of the head group significantly influences the interaction of adjacent side groups. As the side groups are attached to the polymer back bone, tailoring the features of the head group is a potential way to control the conformation of the conjugated polymer back bone.

2.6 Established chromism mechanisms of PDA

2.6.1 Thermochromism

Thermochromatism was the first stimuli response observed for PDA [37] and over the years, efforts have been made to study the mechanism involved. Recent

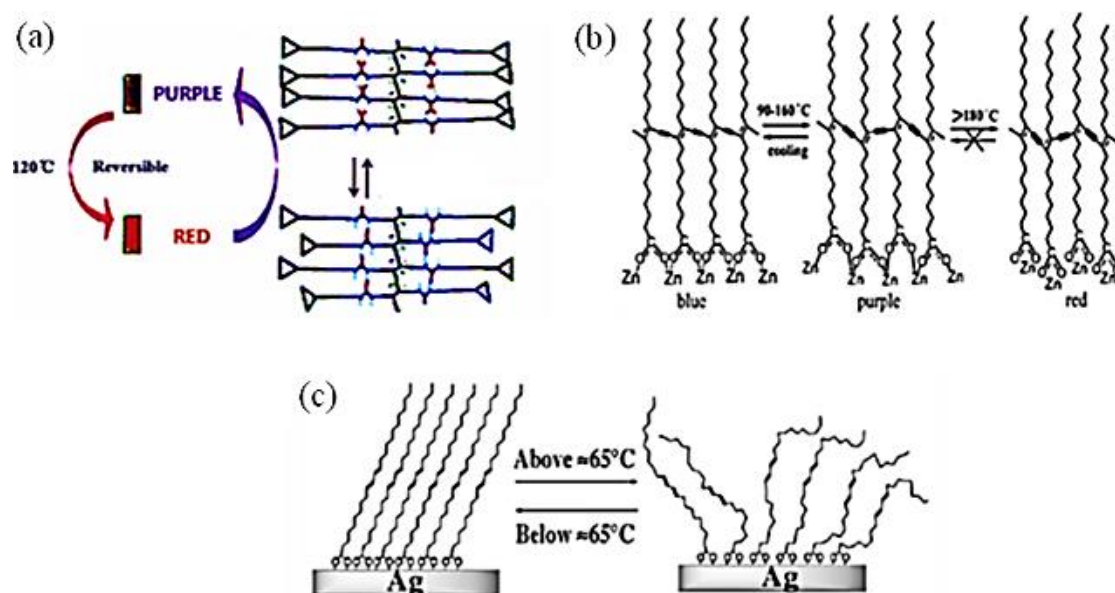


Figure 2.10 Thermochromism in PDA through molecular re-organization, metal co-ordination and organic/inorganic hybrid structures [38, 39, 43].

developments in the field have shown that reversible thermochromism occurs through reversible structural transitions and vice versa [38].

The influence of molecular reorganization on thermochromism is illustrated in Figure 2.10a. FTIR analysis of the samples at different temperatures indicated that cooling from a temperature above 120 °C did not reverse the thermochromic effect. The reason for irreversibility is understood to be the formation of new H-bond networks by urea group.

Study on thermochromism of metal coordinated PDAs showed a significant influence of metal on the resulting chromic effect [43]. Schematic of a possible mechanism of thermochromism between blue and purple states in Zn^{2+} -PDA is illustrated in Figure 2.10b. The color change was attributed to the conversion of triclinic subcell at room temperature to an orthorhombic subcell on heating. As minimum changes were induced in the head groups, the color change was reversible up to 160 °C, which is the highest reported temperature to date.

Organic/inorganic hybrid structures were also capable of reversible thermochromism, as observed by Joo et al. [39]. They studied a system of PDA assembled on silver metal layer and the schematic of the mechanism is shown in Figure 2.10c. A zigzag conformation of PDA chains at room temperature corresponds to the blue phase, which converts to an irregular gauche structure on heating ($\sim 65\text{ }^{\circ}\text{C}$) to yield the red phase. The color change was reversible for Ag surface but irreversible for other surfaces such as silica. The exact influence of the metal layer on reversibility is still unclear.

2.6.2 pH chromism

Jonas et al. [40] pioneered investigations on pH induced chromism in PDAs by fabricating PDA lipids based on hydrazide derivatives. The prepared polymers underwent reversible chromic transitions between blue and red in response to changes in the environment pH. The mechanism involved is illustrated in Figure 2.11. As in the case of many thermochromic systems, the reversibility of color change was attributed to the unique H-bonding pattern of the hydrazide head groups [10]. The explanation was made based on FTIR analysis which indicated substantial differences of bonding structures between neutral hydrazide and the HCl salt.

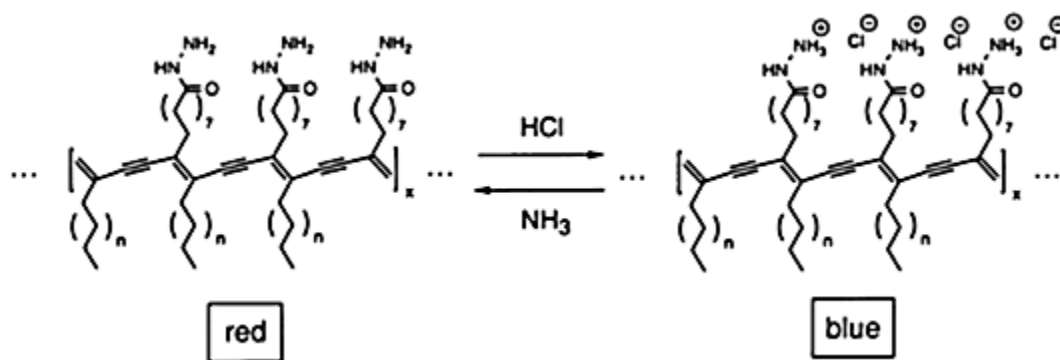


Figure 2.11 Color changes of PDA lipids in presence of HCl or NH_3 [40].

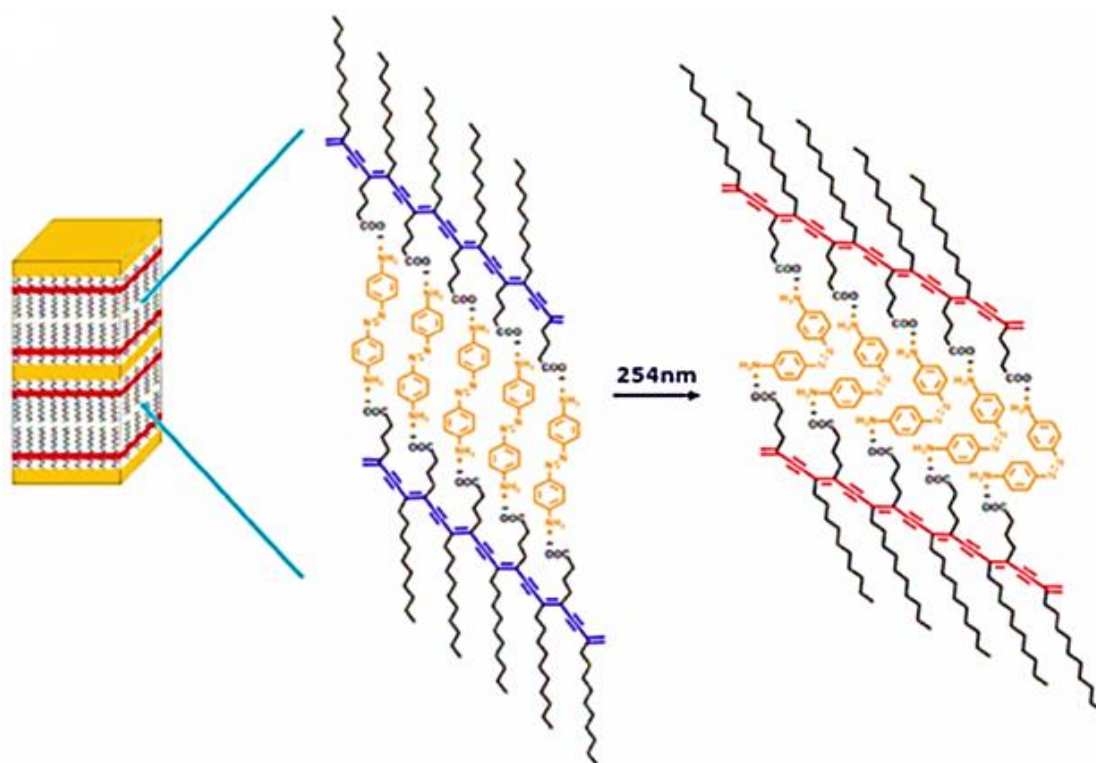


Figure 2.12 Conformation change induced by azobenzene in PDA resulting in color change [41].

2.6.3 Light induced chromism

Azobenzene is known for its unique conformation transition between cis and trans states upon UV irradiation. Peng et al. [41] introduced azobenzene moieties into PDA to realize light induced chromatic transition of the chromatic films. The mechanism of the process is illustrated in Figure 2.12, with azobenzene forming a layered lamellar structure with PDA. UV irradiation causes shortening of azobenzene moieties and results in pulling of neighboring PDA chains. The color change from blue to red was attributed to the decreased conjugation length induced by the pulling action of azobenzene.

2.7 Making PDA chromism reversible

2.7.1 Aromatic interactions

Hammond et al. [42] carried out in depth investigations on thermochromism in PDA formed from DA monomers specifically designed with aromatic groups in the

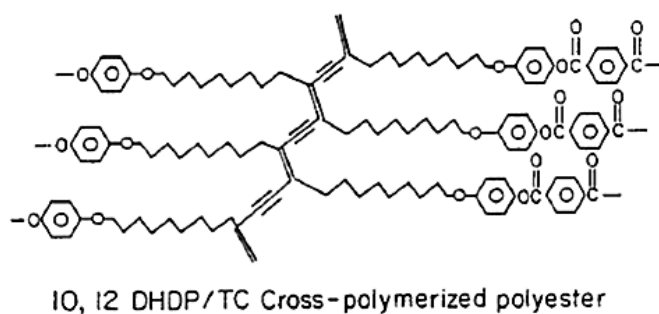


Figure 2.13 Structure showing the strong aromatic links in the polymer resulting from 10,12 DHDP/TC [42].

alkyl side chains. DA monomers 5,7 DODBA, 10,12 DHDP and a polyester formed by polycondensation of 10,12 DHDP with terephthaloyl chloride (TC) were polymerized to yield corresponding thermochromic PDAs.

While all resulting PDA films showed thermochromism, only the 10,12-DHDP/TC cross polymer showed signs of reversibility upon cooling to 50 °C. The authors attributed this apparent difference in reversibility between the PDA films to the differences in linkage between the rigid mesogenic side chains. While PDA from 5,7 DODBA and 10,12 DHDP head groups were linked merely through associative interactions of H-bonds, that of 10,12 DHDP/TC were linked by three covalently bonded aromatic rings as illustrated in Figure 2.13.

2.7.2 Covalent interactions

Peng et al. [43, 44] synthesized PDA/Silica nanocomposite thin films with tunable and reversible thermochromism through a sol-gel assembly process. A typical structure for one such monomer and the subsequent polymerized form is shown in Figure 2.14. The hydrolysis and condensation reactions of ethoxysilane groups in these systems helped restore the original chain conformation on removal of thermal stimulus leading to reversibility of the blue to red transition. It was also found that enhanced flexibility of the side chains, governed by the number of methyl spacers, improved reversibility in these systems in general. The strong covalent links of the head groups

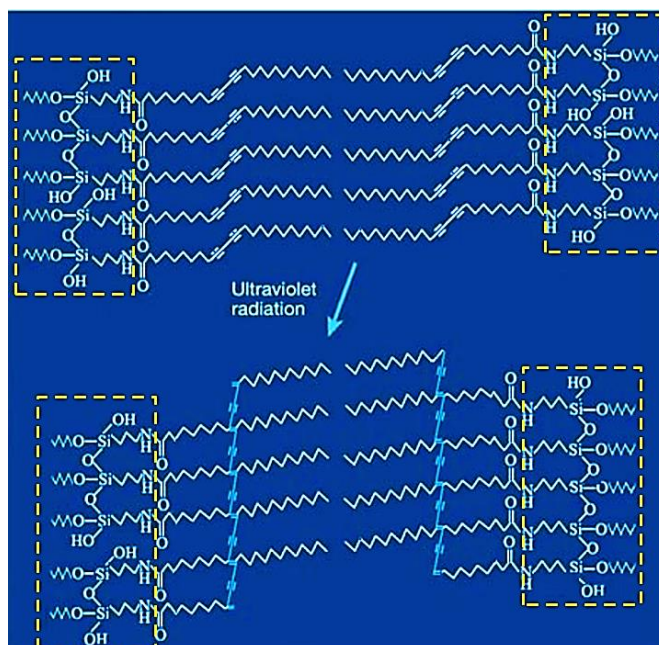


Figure 2.14 Designed diacetylene silicate species with strong covalent head group links with inorganic silica framework [44].

with silica also significantly enhanced the thermal stability of the resulting PDA, with thermochromism occurring as high as 113 °C as opposed to 77 °C for PDA systems based on non-covalently interacting head groups.

2.7.3 Hydrogen bonds

The earliest attempts to improve reversibility of chromatic transitions in PDA were based on influencing the hydrogen bond interactions of the head groups. Song et al. [45] synthesized bolaamphiphilic DA lipids with different head groups, intentionally varying the extent of H-bonding capability, as shown in Figure 2.15a. While PDA resulting from 1 was least likely to form H-bonds, PDA from 3 was expected to have strong H-bonds. Even a slight change in temperature (from room temperature to ~35 °C) caused an irreversible color change in PDA-1 while PDA-2 gave similar chromatic response only beyond 90 °C. The authors attributed this difference to the enhanced H-bonds in the structure of PDA-2, proposing that strong H-bonds are crucial to facilitate reversible chromatic transitions in PDA.

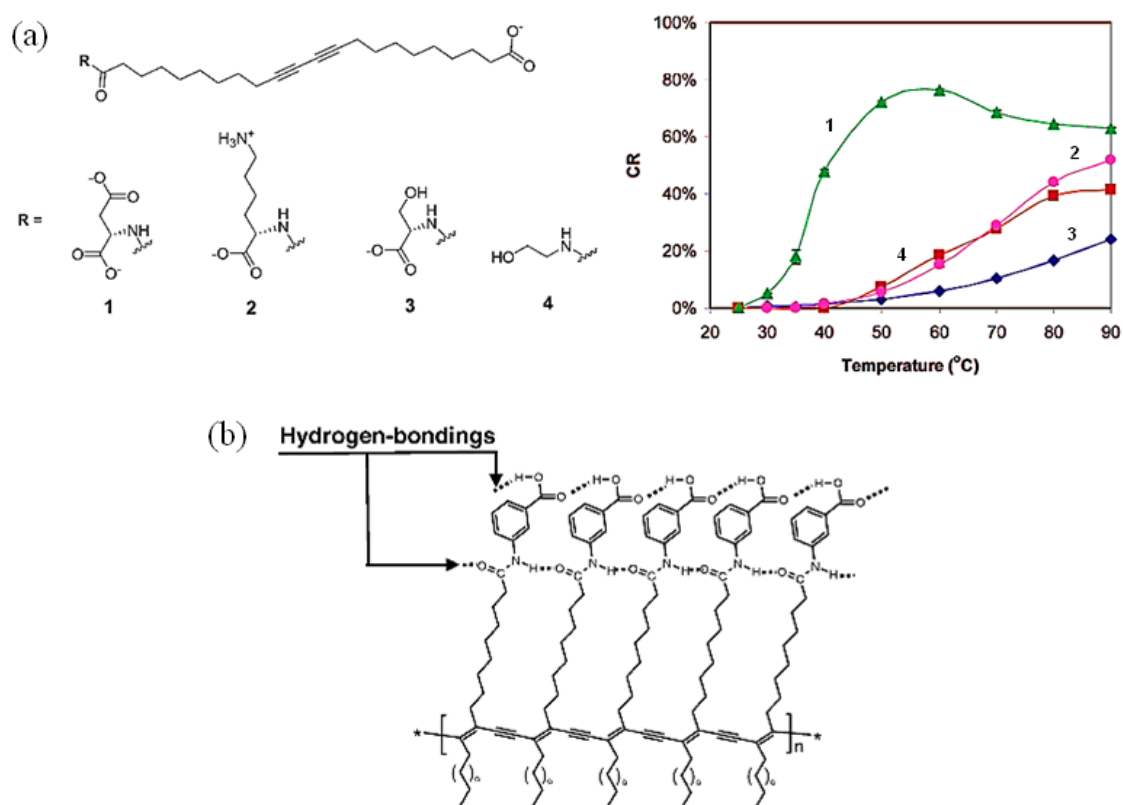


Figure 2.15 (a) DA monomers with different head groups 1-4 and the chromatic response of resulting PDAs (right) and (b) enhanced H-bonds by incorporating functional groups capable of H-bonding onto conventional PDA [45, 46].

Dong et al. [46] carried out another elegant investigation of the effects of H-bonds on PDA chromism. They added functional groups capable of H-bonding to conventional PDA, hoping to improve the overall H-bonding in the system, to meet the criterion for reversibility (Figure 2.15b). Their approach worked with the PDA resulting from DA derivative containing an un-substituted anilide group and carboxy substituted meta anilide group, with rigid intra and inter molecular H-bonds demonstrating rapid reversibility.

2.7.4 Metal ion effect

The influence of metal ions such as Zn^{2+} , Ag^+ and Cu^{2+} in the sub phase of DA monomers on the thermochromism of subsequent PDA films were investigated by Huang et al. [47]. They found that Zn coordinated thin films of DA yielded the blue

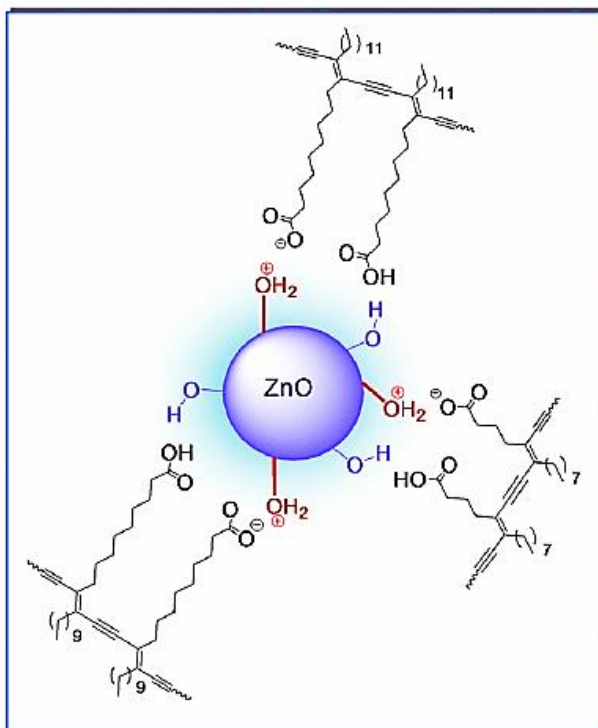


Figure 2.16 Different modes of interaction of PDA head groups with ZnO surface [48].

phase on polymerization and reversibly switched between the blue and purple state upon thermal stimulation. The improved reversibility in these systems was attributed to strong ionic interactions and H-bonding at the ZnO interface (Figure 2.16), which restricts the dynamics of alkyl side chains and promotes PDA ordering, which in turn drastically alter the thermochromics behavior of the resulting PDA.

More recent investigations of PDA-ZnO and PDA-ZnO/ZrO₂ alloys by Patolla et al. [48] demonstrated the ability to control the speed of thermochromic reversibility in these systems. Compared to the other forms of PDA modifications to improve reversibility of the chromatic transition, this method based on metal ions stands out owing to its simplicity.

Thus, chromism in PDAs appears to be a complicated phase transition process influenced by numerous factors such as chain length, head group architecture and substrate interactions, to name a few. While the types of PDA chromism discussed so

far were intrinsic to PDA, electrochromic blue to red transitions were reported only for carbon nanotube (CNT)-PDA composite fibers and sheets. Hence, there appears to be some unique chemistry between CNTs and PDAs that invoke electrochromism in PDAs. The following sections summarize the basics of carbon nanotubes and its assemblies, which is essential for further investigation of CNT-PDA electrochromism.

2.8 Basics of carbon nanotubes

Diamond, graphite and amorphous carbon are the three standard forms of carbon. However, elemental carbon in the sp^2 hybridization can form a variety of amazing structures [49]. Buckminsterfullerene C_{60} was the first of such structures to be discovered by a team headed by Smalley, Kroto and coworkers in 1985 and lead to the nobel prize in chemistry in 1997 [50]. In 1991, Iijima reported quasi one dimensional nanotubes when he observed multi walled carbon nanotubes (MWCNTs) in carbon soot prepared by an arc discharge method, which captured the attention of scientists worldwide because of the remarkable 1D quantum effects predicted for their electronic properties (Figure 2.17) [51]. It was also predicted that the excellent structural properties of CNTs might give rise to some unique applications [52].

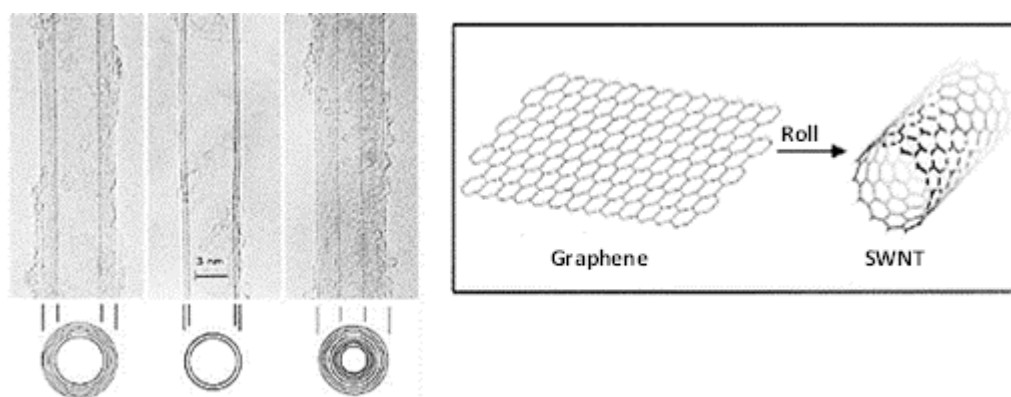


Figure 2.17 TEM images of MWCNT (left) and illustration of conversion of graphene sheet to CNT (right) [52].

The planar, aromatic sp^2 -bonded carbon framework makes graphene and graphite chemically inert. Fullerenes on the other hand are extremely reactive [53]. The tremendous difference in reactivity of these two forms of carbon is based on the introduction of strain by bending of planar graphene in two dimensions to form a fullerene [54].

Fullerenes and CNTs differ in their curvature, with fullerenes curved in two dimensions and CNTs, only in one. In such non-planar conjugated structures, reactivity is determined by: i) curvature induced pyramidalization (Figure 2.18a) and ii) π -orbital misalignment of adjacent carbon atoms (Figure 2.18b). Reactivity of fullerenes is driven by release of pyramidalization strain energy based on rehybridization of sp^2 carbon atom into sp^3 carbon atom. As the distortion in CNTs is lower, the reactivity is significantly lower than fullerenes. It should be noted that the fullerene-like end caps of CNTs are more susceptible towards reactions compared to the planar sidewalls.

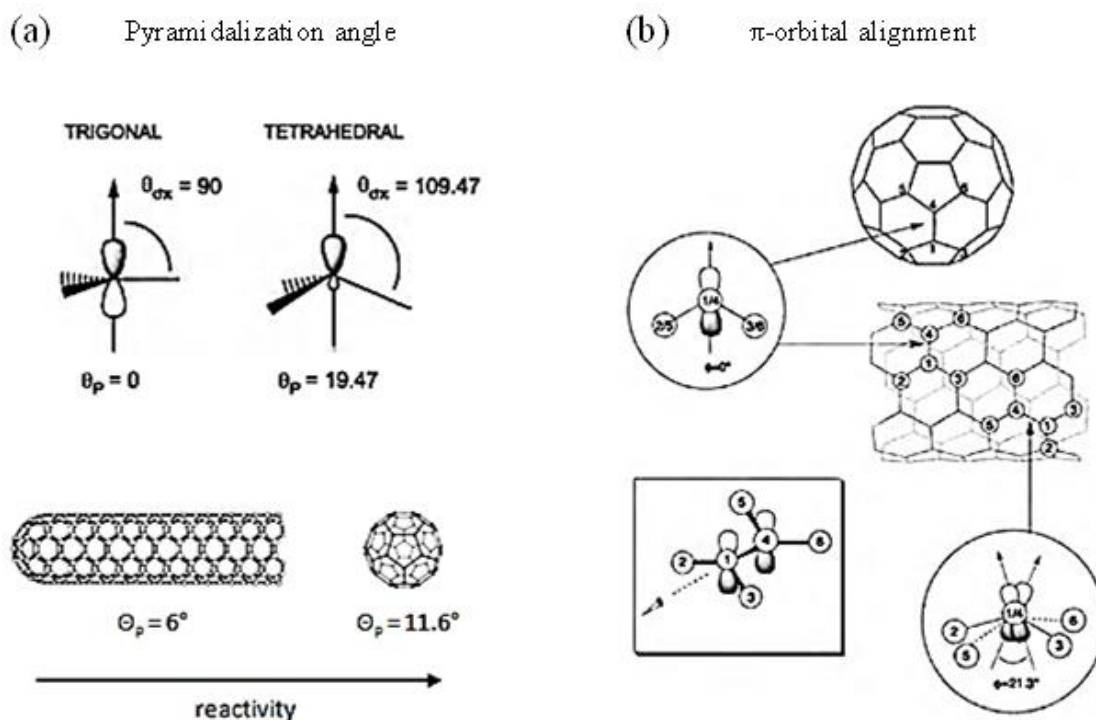


Figure 2.18 (a) Comparison of pyramidalization angle and (b) π -orbital misalignment in CNTs and fullerene C₆₀ [53, 54].

The π -orbital misalignment is significant in the case of CNTs while it is negligible in the case of fullerenes. Consequently, reactivity of CNTs is governed by this parameter. There exists two sets of different bonds in CNTs: one type runs parallel to the circumference with $\phi = 0^\circ$ while the other set of bonds exhibits an angle to the circumference with $\phi = 21.3^\circ$. This misalignment generates torsional strain in CNTs, the release of which drives addition reactions.

2.9 From Aligned CNTs to macroscopic assemblies

It was common knowledge that practical applications of CNTs would require highly aligned assemblies of CNTs. The first significant report of such imposed alignment in CNTs was by Ajayan et al. [55] wherein the alignment was induced by cutting thin slices (50 – 200 nm) of a nanotube-polymer composite (Figure 2-19a and b). The CNTs in the slices were more or less parallel, allowing for the first time the potential measurement of individual CNT properties. Selective etching of the polymer matrix could reveal aligned patterns of individual CNTs, which could be ideal substrate patterns for one dimensional nanostructures.

However, such an approach of imposing CNT alignment through a polymeric phase has undesirable side-effects. For instance, the degree of orientation of CNTs is affected by thickness of slices and increasing slice thickness hinders alignment. Moreover, the insulating resin matrix in itself is undesirable for potential applications. Li et al. [56] employed chemical vapor deposition (CVD) to grow aligned CNTs over large areas, with no insulating polymer phase such as PVA. Although CVD had been used previously for various applications, typical substrates used were carbon black, graphite and silica coated with transition metal oxides. Li's team used mesoporous silica embedded with iron nanoparticles as the substrate, which yielded vertically aligned CNTs upon decomposition of acetylene onto the activated nano catalyst (Figure 2.19c

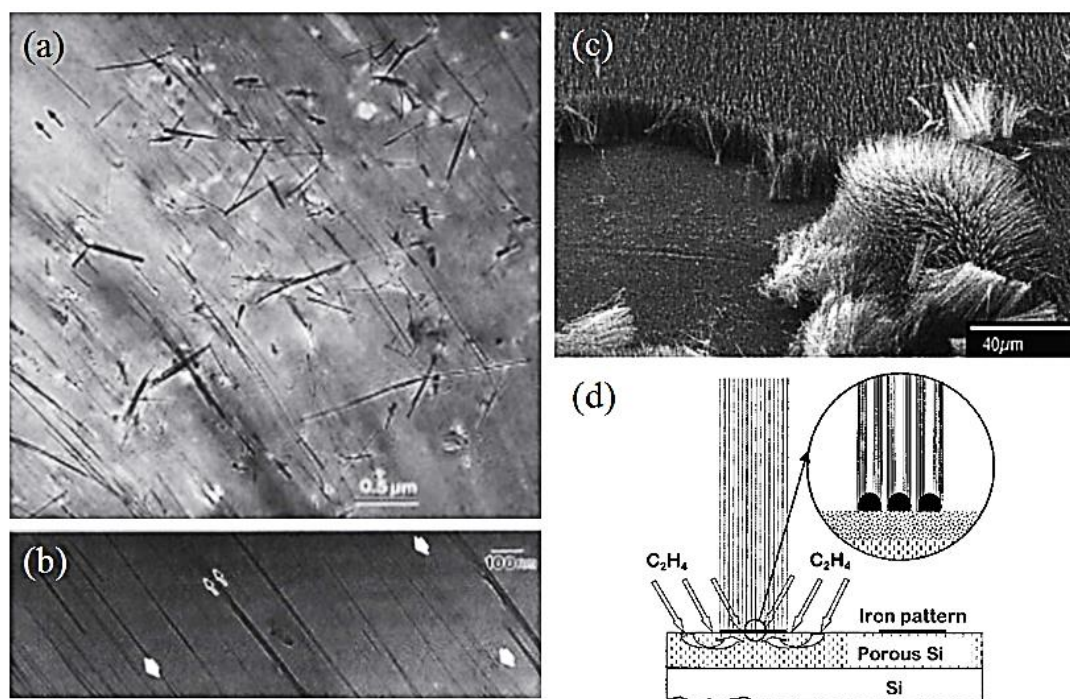


Figure 2.19 (a) Slice of CNT incorporated PVA, (b) high magnification image showing aligned CNTs in PVA, (c) aligned CNT grown using CVD and (d) growth mechanism of CNT forests [55-58].

and d). The growth was believed to proceed primarily through base mode although certain CNT segments gave evidence for tip growth mode as well. In contrast to Ajayan's work, this method offered the potential to grow CNTs that are aligned, isolated and long, over large areas by tuning the parameters during growth. This tremendously increased the odds of fundamental research and applications resulting from isolated and aligned assemblies of CNTs.

Following a similar approach to Li's, Ren et al. [57] demonstrated CVD growth of aligned CNTs with tunable diameters from 20 – 400 nm and lengths of 0.1 – 50 μm, using nickel coated glass as the substrate. Patterned substrates have also resulted in vertically aligned CNT forests with excellent control over the spacing and density of CNTs [58].

As with the case of many significant scientific discoveries, the phenomenon of self-assembly of carbon nanotubes into yarns was stumbled upon in the laboratory by a group of researchers headed by Shoushan Fan, in 2002 [59]. They demonstrated that CNT yarns could be drawn out from super aligned CNT arrays to lengths of up to 30 cm and subjected to post spin heat treatments to enhance strength and conductivity (Figure 2.20). They found that only super-aligned CNT forests in which individual CNTs stick together with high van der Waals interactions could be spun into macroscopic yarns. Moreover, the size of the tool tip used to draw the initial ribbon out from the forest determined the dimensions of the resulting yarn. To date, this method remains the most straight forward means of transforming individual CNTs into a macroscopic form factor.

Following the pioneering work of Jiang et al. [59], many other research groups reported drawable CNT forests. The drawability of these forests were attributed primarily to van der Waals interactions. However, it is to be noted that though aligned

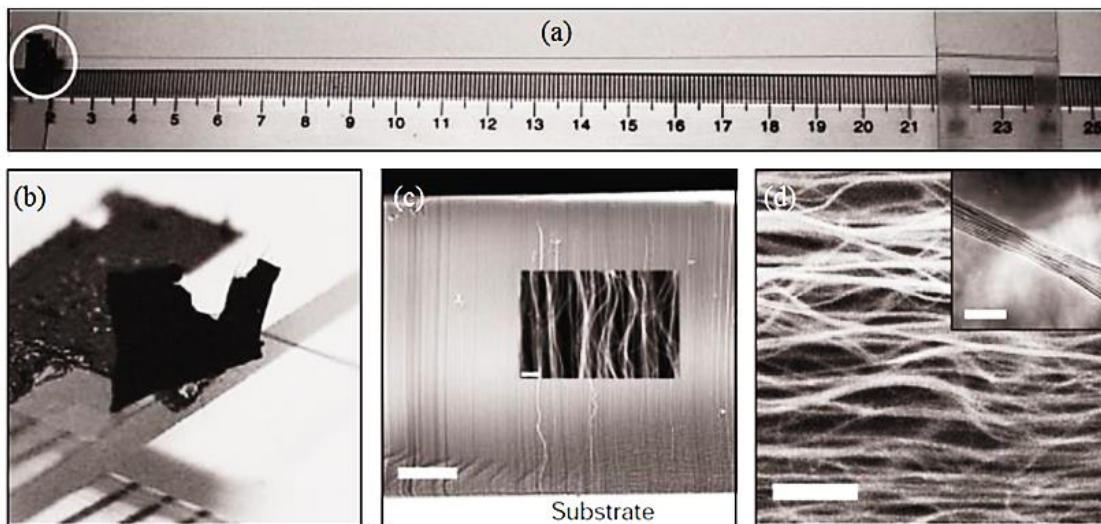


Figure 2.20 (a) Dry spun CNT yarn, (b) close up of yarn pulled out from free standing CNT forest, (c) SEM images highlighting super aligned nature of drawable CNT forests (scale bar: 100 μm , inset: 200 nm) and (d) SEM of yarn; inset shows the TEM of a single thread of the yarn (scale bars: 500 nm, inset: 100 nm) [59].

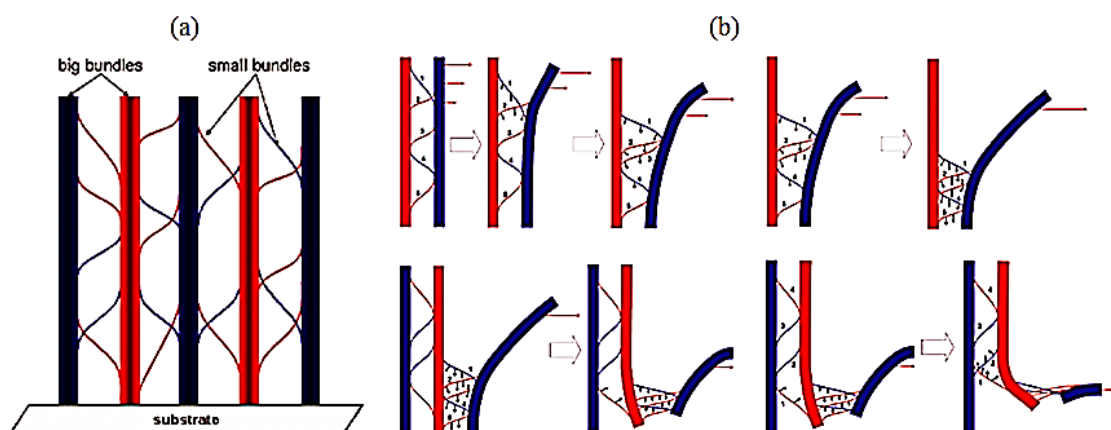


Figure 2.21 (a) Schematic illustrating the presence of interconnections between CNT bundles and (b) the unzipping and strengthening of interconnections at the bottom of the forest upon drawing [60].

CNT forests could be grown using a wide range of growth conditions, only forests that fell within a strict window of forest heights and densities were drawable. Hence, van der Waals forces alone, which exists for both drawable and non-drawable forests, cannot explain drawability of CNT forests. The most comprehensive structural model for drawability of CNT forests was reported by Zakhidov et al. [60]. They attributed drawability of CNT forests to a special network of interconnections between bundles. The unzipping of interconnections upon peeling off initial bundles from the CNT forests as well as the self-strengthening of the interconnections at the top and bottom of the forests as a consequence of multiple unzipping processes, work together to yield long CNT yarns (Figure 2.21).

2.10 Electron transport in CNT yarns

The electrical resistivity of CNT yarns are typically two orders of magnitude higher than individual CNTs. It is believed that this discrepancy may arise from high impurity content (amorphous carbon and catalyst particles) and contact resistances between CNTs in the assembled yarn. A systematic approach to investigate mode of electron transport in dry spun yarns of CNT was carried out by Li et al. [61]. They found

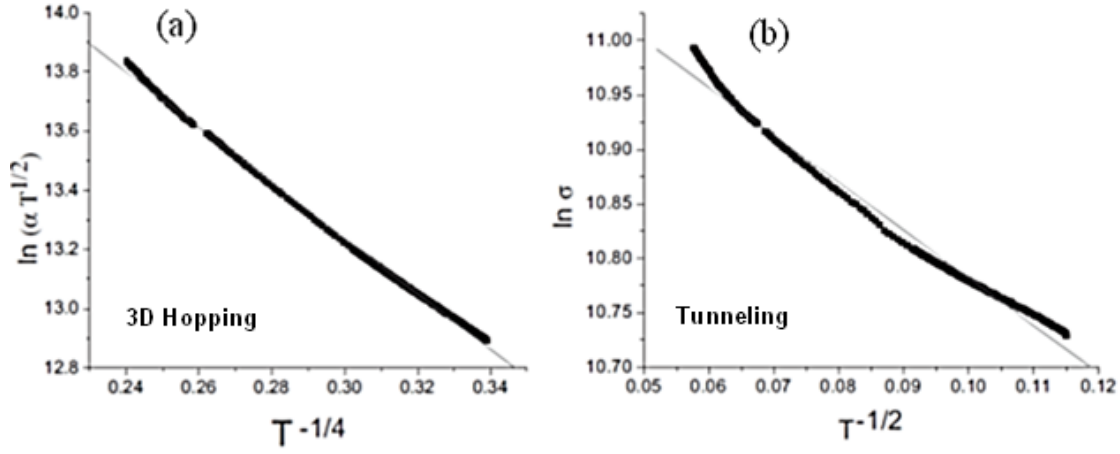


Figure 2.22 Comparison of fits for hopping and tunneling conduction in CNT yarns. Better fit for the hopping model is obvious [61].

that yarns from tall CNT forests gave lower resistivities than those from short forests, supporting the idea that inter CNT connections do indeed increase resistivity of CNT assemblies [62].

Two methods are typically used to describe conduction of CNTs: variable range hopping (VRH) and tunneling conductance (TC), both of which can be described using the following equations:

$$\sigma T^{1/2} = \exp\left(\frac{-B}{T^{1/4}}\right) \quad (2.11)$$

$$\sigma = \sigma_0 \exp\left(\frac{-A}{T^{1/2}}\right) \quad (2.12)$$

where, σ is the electrical conductivity, σ_0 , A and B are constants, and T is absolute temperature. The fit of $\ln(\sigma T^{1/2})$ versus $T^{-1/4}$ was way better, suggesting a conduction mode in CNT yarns dominated by 3D hopping (Figure 2.22). The authors attributed the hopping preference to the defects present in CNT yarns. Defects prevent electrons from being confined in the 1D channels of CNTs and promote hopping from one defect site to another, even across neighboring CNT bundles. Further, they found that mild chemical treatments of CNT yarns which do not destroy the planar π -conjugated

structure of CNTs could significantly improve the hopping conductivity of these assemblies.

2.11 Foreign molecule interaction with CNTs

Along with high conductivity, CNTs are known to exhibit other excellent properties such as good thermal and chemical stability, high tensile strength and elasticity and the ability to adsorb gas molecules, to name a few. However, the aggregation of CNTs into bundles of varying diameters, variation in lengths, diameters and helicity of nanotubes and creation of defects at nanotube ends and surfaces, have hindered attempts to put the potentially excellent features of CNTs into practical use [63]. Attaching chemical functionalities onto the surface of CNTs can solve this problem and allow combination of unique properties of CNTs with other types of materials like polymers [64].

Foreign molecules can interact with CNTs via covalent or non-covalent interactions (Figure 2.23). Covalent functionalization of CNTs involve the formation of

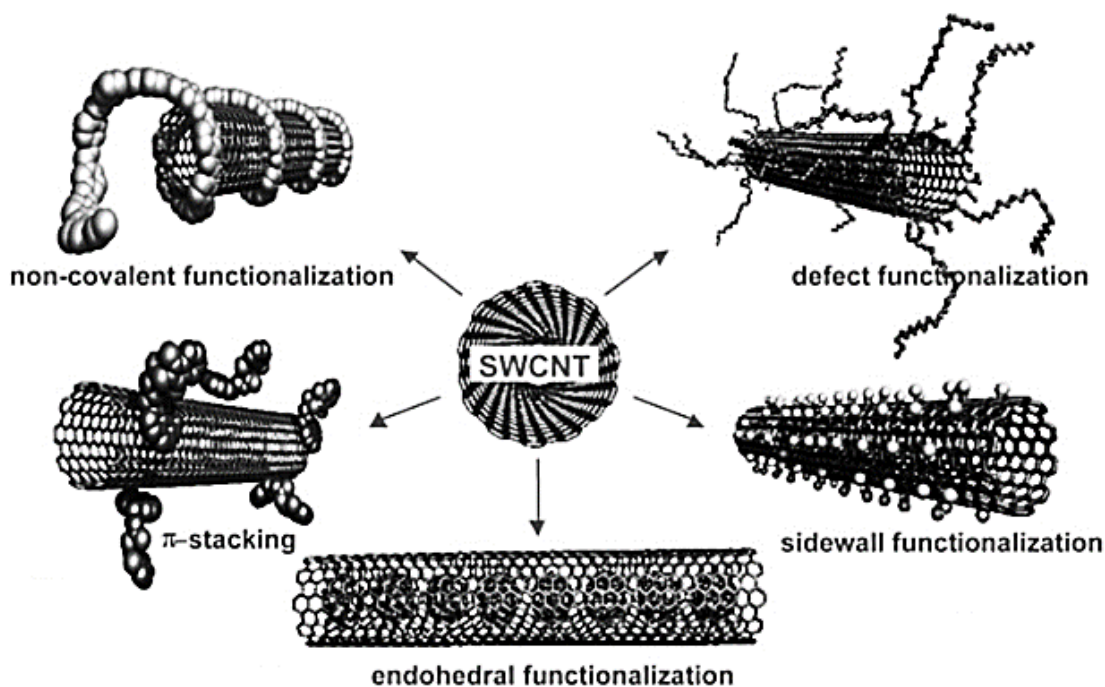


Figure 2.23 Different modes of functionalization of SWCNTs [64].

covalent linkages between functional entities with the carbon scaffold of CNTs. Non-covalent functionalization is based on surface adsorption forces such as Van der Waals forces and π -stacking interactions. Defects present on the surface of CNTs can also form sites for functionalization. Apart from these exohedral derivatizations, under special circumstances, atoms or molecules can occupy the interior of CNTs to realize endohedral functionalization. A brief overview of the different strategies employed to functionalize CNTs is provided next.

2.11.1 Covalent interactions of molecules with CNT

Covalent attachment of functional entities on the CNT can take place at the termini of the tubes and/or at the sidewalls. Covalent functionalization directly on CNT sidewalls requires re-hybridization of one or more sp^2 carbon atoms to sp^3 hybridization, destroying conjugation. Extensive studies into the chemistry of CNTs have resulted in development of methods for halogenation [65, 66], addition of radicals [67], electrophiles [68] and nucleophiles [69], addition of inorganic compounds [70] and ozonolysis [71] of CNT surfaces.

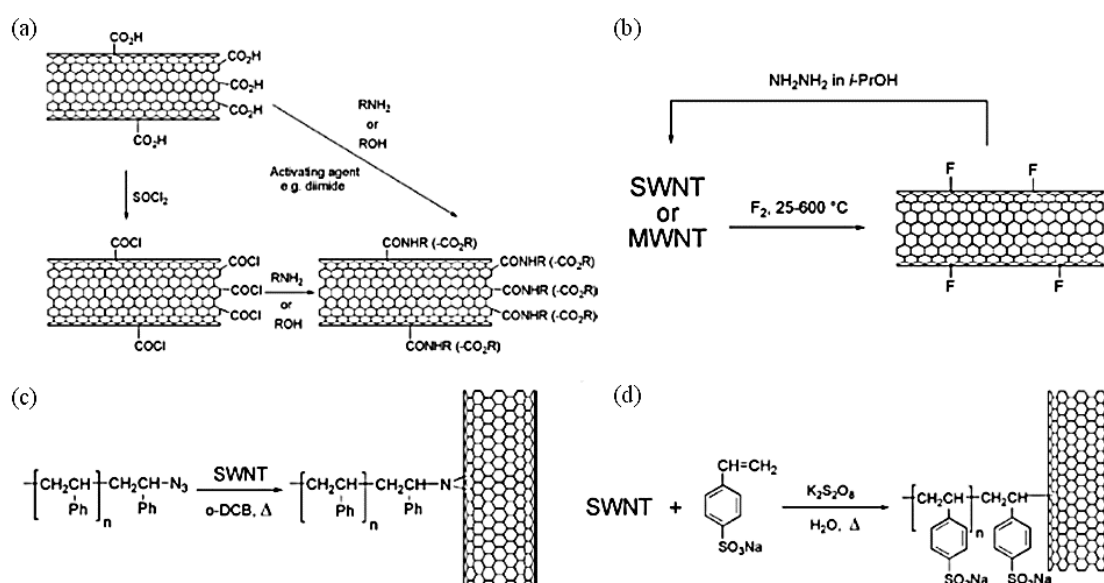


Figure 2.24 (a) Reaction schemes for defect-site derivatization, (b) fluorination and defluorination, (c) 'grafting to' approach and (d) 'grafting from' approach of CNTs [66-71].

Covalent functionalization may also be realized by chemically transforming defect sites, intrinsically present or intentionally introduced by surface oxidation. The various defects associated with CNTs are pentagon-heptagon defects, Stone-Wales defects, sp^3 defects saturated with hydrogen or other groups, vacancies with dangling bonds and open tube ends terminated with carboxylic acid functionalities [72].

Grafting of polymers onto CNT surface has also been reported with two approaches being used, namely ‘grafting to’ and ‘grafting from’ [73]. The first approach relies on synthesis of polymer of specific molecular weight followed by attachment onto CNT surface. ‘Grafting from’ is carried out by immobilizing monomers on the CNT surface, followed by polymerization of the monomer species. Figure 2.24 illustrates some of the mechanisms of covalent functionalization of CNTs discussed so far.

2.11.2 Non-covalent interactions of molecules with CNT

It has been suggested that covalent bonding is favored on the exterior of CNTs while non-covalent interactions favor endohedral adsorption [74]. Gas molecules have been found to adsorb non-covalently on numerous adsorption sites available on the surface of bundles of CNTs (Figure 2.25a). Studies on the energetic of He dispersion on surface of CNTs indicated a binding energy 60 % higher than that of planar graphite, though the contribution of binding energy from surface sites and interior of CNTs couldn’t be distinguished [75]. However, Ne, Xe and CH_4 were found to adsorb specifically on groove sites with binding energy greater 75% higher than planar graphite [76, 77].

A study of gas phase adsorption of organic molecules on CNTs showed that the interaction of π -electrons of the molecule with the electronic system of CNT played a crucial role [78]. The conclusion was reached on comparing adsorption energies of organic systems, which increased when π -electrons increased from 0 (cyclohexene) to 6 (benzene) (Figure 2.25b).

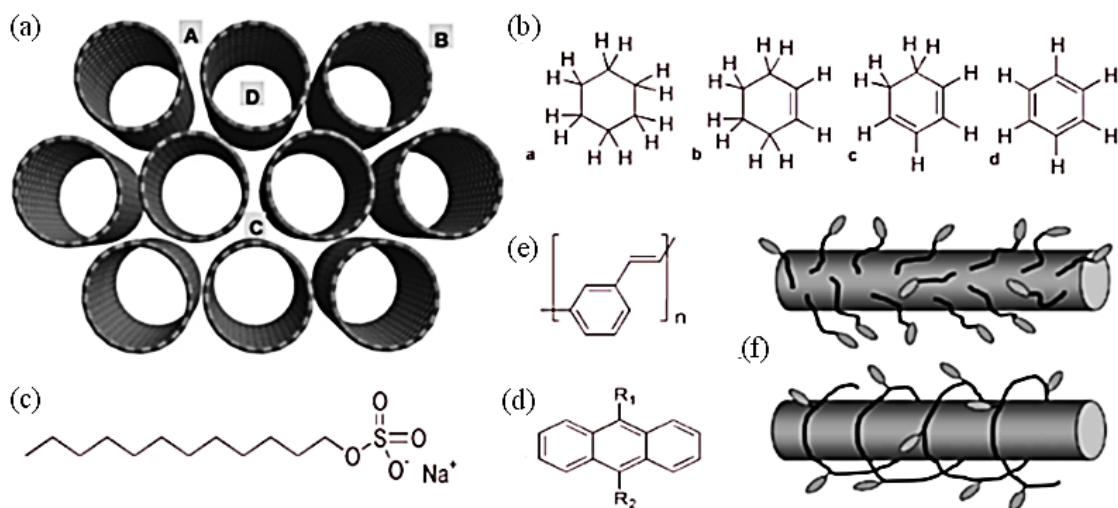


Figure 2.25 a) Adsorption sites in CNT bundles: A-grooves of bundles, B-outer surface of sidewalls, C-interstitial cavities and D-nanotube cavities, b) cyclic molecules with varying π -electrons), c)-e) represents different adsorbed molecules on CNT surface and f) micelle formation by small molecules (top) and helical wrapping by polymers (bottom) [74-78].

Amphiphilic molecules (surfactants) have also been known to interact non-covalently with CNT surfaces (Figure 2.25c and d). Charged surfactants form micelles on CNT surface which repel each other electrostatically while charge neutral surfactants form a large solvation cell around CNT surface [79, 80]. It was also established that the micelles formed in the first case follow no specific structural organization and are weakly bound to the surface. Longer and branched alkyl groups improves adherence of these charged surfactants on the surface of CNTs [81].

The extremely good adherence of aromatic systems like pyrene and anthracene on CNT surfaces have been investigated previously and attributed to π -stacking effect [74]. Understandably, presence of aromatic groups in the surfactant (sodium dodecylbenzene sulfonate SDBS) seemed to produce more specific and directional interactions with the CNT surface due to π - π stacking effect.

While small molecules form micelles, polymers tend to form helical coils around CNTs. This is to minimize strain induced by mechanically rigid CNTs which tend to

cause polymers to take up energetically unfavorable configurations [82]. A comparison of micelle formation by small molecular surfactants and helical wrapping by long chain polymers is shown in Figure 2.25f.

In terms of the chemistry involved, sidewall covalent functionalization of CNTs is accompanied with a change of hybridization from sp^2 to sp^3 and a simultaneous loss of conjugation. Consequently, covalently functionalized CNTs will have different electrical and mechanical properties than pure CNTs. Non-covalent functionalization does not alter the intrinsic properties of CNTs as it does not destroy the conjugation structure. Hence, for applications focusing on combining the desirable electrical properties of CNTs with other polymeric species, non-covalent functionalization, specifically polymer wrapping appears to be the best way forward.

J.N. Coleman and colleagues carried out spectroscopic studies to examine the effect of interaction of flexible conjugated polymer (PmPV) with CNTs [83]. Absorption spectrum of the composite was compared with that of neat polymer and pure SWNT and the following observations were made: i) a blue shift of the low energy peak from 3 eV in the polymer to 3.15 eV in the composite and ii) splitting of the 3.7 eV peak in the polymer into two features at 3.64 eV and 4 eV respectively in the composite

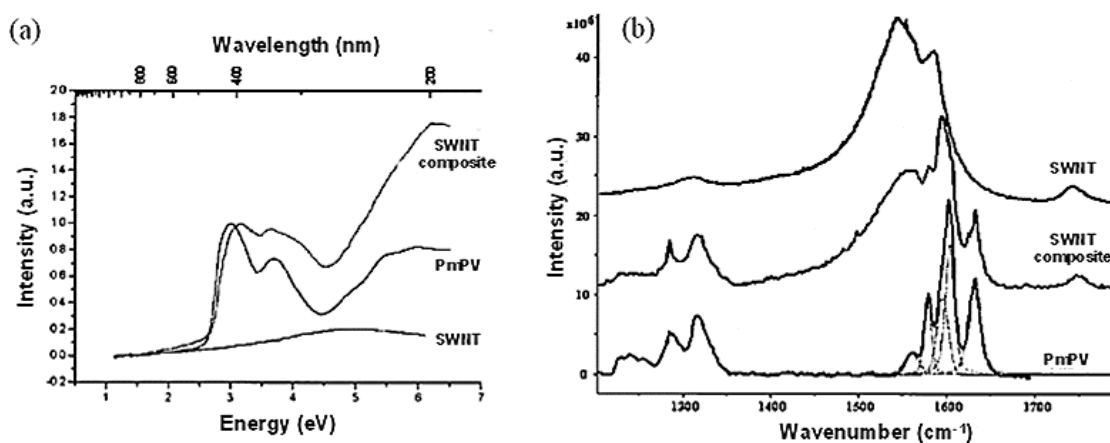


Figure 2.26 (a) Comparison of Absorption spectra and (b) Raman spectra of pure SWNT, PmPVA and SWNT composite [83].

(Figure 2.26a). The first observation was found to be consistent with reduction in electron delocalization along the polymer chain due to binding of the polymer onto the nanotube, as suggested first by Ago et al. [84].

The original peak at 3.7 eV in the pure polymer is believed to be due to broken charge conjugation symmetry in the polymer. Hence, the second observation is ascribed to further disruption in the conjugation symmetry brought about by curvature imposed on the polymer due to the presence of SWNT.

In the same study, Raman spectrum of pure polymer, SWCNT and polymer-SWCNT composite were compared to investigate structure-property relationship in both components (Figure 2.26b). Incorporation of SWNTs cause two main changes in the spectrum compared to neat polymer: i) evolution of the broad band at 1627 cm^{-1} to two well defined features and ii) changes in relative intensities of the modes at 1610 cm^{-1} and 1590 cm^{-1} . These changes indicate alteration of the vibrational structure of the polymer due to binding onto SWNT lattice and are evidences for the strong alteration of polymer conformation due to interaction with nanotube.

2.11.3 Dependence of polymer structure

Yang et al. [85] carried out molecular dynamics simulation studies on SWCNTs and their interaction with individual molecules of various monomers with the intention of understanding the influence of monomer structure on the process (Figure 2.27). All the monomer systems considered showed a general tendency to adhere to the surface of CNTs, with monomers having aromatic rings on the backbone (PPV and PmPV), showing stronger interaction energy than monomers with aromatic rings on the side chain.

It was also understood that the high curvature or low diameter CNTs were not conducive for polymer adhesion as the interaction energy between all the monomers and CNTs increased monotonously towards an asymptotic value given by interaction of

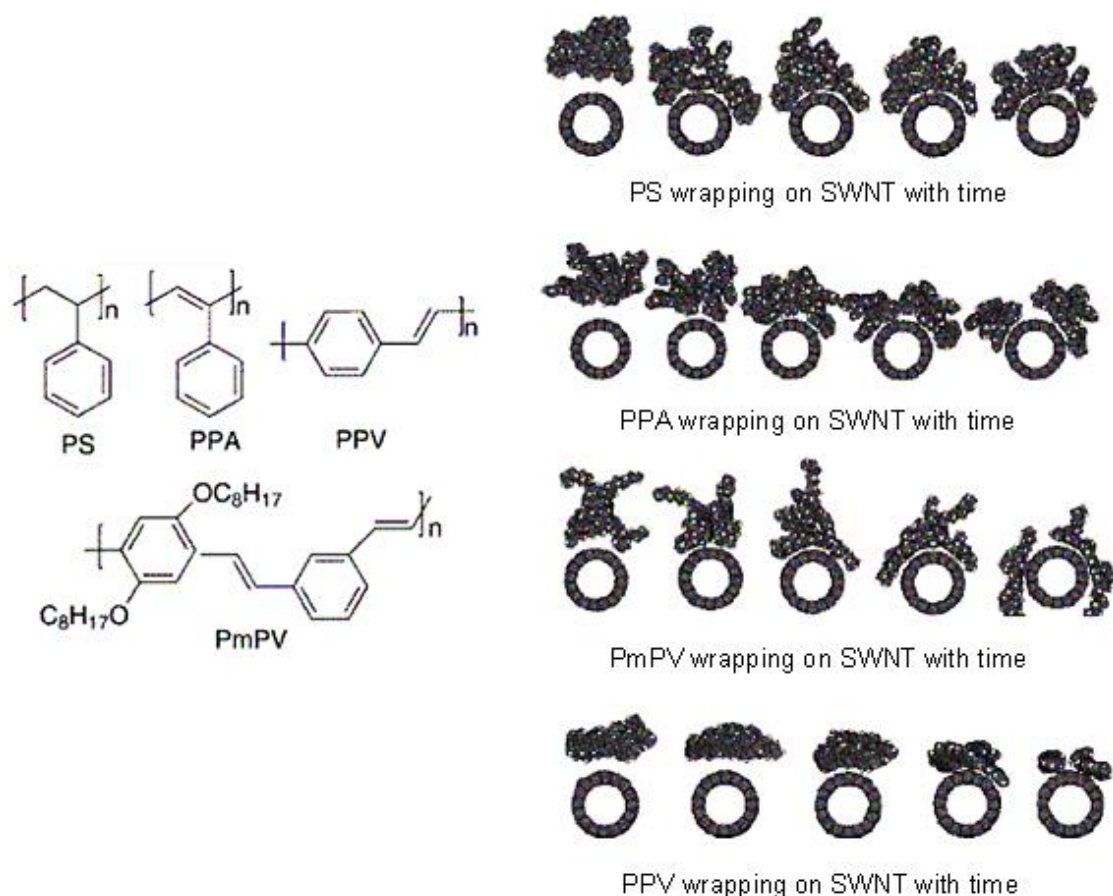


Figure 2.27 Structures of monomers (left) and wrapping tendency on SWCNTs (right) [85].

polymer with flat graphite surface. Moreover, aromatic rings on the side chains tend to align perpendicular to the tube surface while aromatic groups in the backbone are aligned parallel to the surface of CNT.

Studies based on change in mean radius of the polymers, which is the mean square distance of the polymer atoms from the center of mass of the polymer chain, indicated that polymers with flexible backbone (PmPV) aligns along the surface of CNT while the rigid ones do not stretch out on the surface. The efficiency of polymer wrapping for the different monomer structures was studied and it was observed that only flexible monomers with aromatic groups along backbone (PmPV) showed the tendency to follow a conformation parallel to the axis of nanotubes (Figure 2.27).

In summary, literature suggests that not only can conjugated polymers be covalently or non-covalently adhered onto CNTs, they exhibit complex interactions based on the structural properties of the CNTs as well as the polymer under consideration. In the following sections, the fundamental properties of PDA, the conducting polymer phase responsible for color change in electrochromic CNT-PDA composites, are reviewed.

2.12 What we know about CNT-PDA electrochromism

A family of novel nanocomposites with electrochromism was developed by Peng et al. [9] by incorporating carbon nanotubes (CNTs) with PDA. The composites changed color from blue to red on passage of current in a very short time (~ 2 s) as shown in Figure 2.28. The mechanism was proposed to be most likely due to the interaction of CNTs with PDA and the three dimensional hopping of electrons from one nanotube to neighbouring ones. The electric field generated between nanotubes is assumed to cause polarization of the polar head groups of PDA which induces conformation changes in PDA resulting in color change [10].

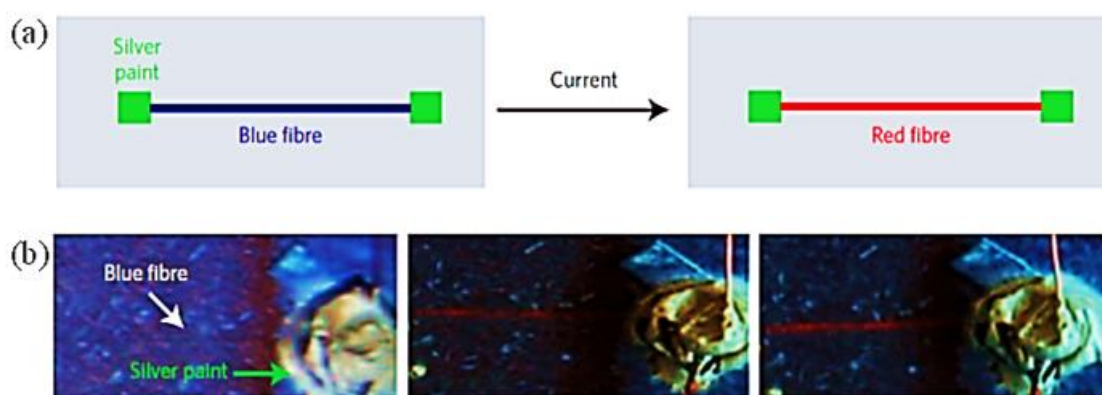


Figure 2.28 (a) Schematic illustration of electrochromism in CNT-PDA yarns and (b) photographs of blue CNT-PDA yarn turning red under 10 mA current for 2 secs [9].

It is important to note that the current transport properties in CNT/PDA composites is not straight forward as it seems. For instance, not only do electrons hop from one nanotube to a neighboring nanotube, but also to neighboring PDA chains. Similar to the hopping charge transport in CNT yarns (discussed elaborately in section 2.3), charge transport in PDA is also expected to be through hopping of electrons, described by the equation:

$$\phi = A \exp\left(\frac{-B}{T^{\frac{1}{4}}}\right), \quad (2.13)$$

where ϕ is the conductivity, A and B are constants and T is absolute temperature. This distinct temperature dependence is a signature of hopping conductance and distinguishes it from conduction due to thermal excitation [86].

Essentially, CNT yarns substantially increase the hopping sites within the PDA crystalline matrix/domains. This implies that the concentration of PDA and CNTs could have significant effects on the charge transport properties of the composite and the electrochromic effect exhibited. Work towards understanding the influence of CNTs on the polymer in these composites requires knowledge of the fundamental chemistry of CNTs as well as PDA.

Chapter 3 Materials and experiments

3.1 Materials

The horizontally aligned multiwalled carbon nanotube (MWCNT) sheets used towards this thesis was drawn from vertically aligned MWCNT forests grown on a Fe- Al_2O_3 catalyst system. The catalyst was activated at 750° C in a thermal chemical vapor deposition (CVD) reactor and exposed to the carbon source, ethylene, initiating vertical growth of MWCNTs. While MWCNT forest growth occurred over a broad range of growth conditions, MWCNT sheets could be drawn only from forests of specific heights. The experimental details and parameter optimizations to yield drawable MWCNT forests are elaborated in Chapter 4. Diacetylene monomer 10,12-Pentacosadiynoic Acid (PCDA), solvent tetrahydrofuran (THF) and zinc oxide nanoparticles (<100 nm size) was purchased from Sigma Aldrich, Singapore. A 4-Watt UV-254 nm lamp was used to initiate polymerization of DA. The extent of polymerization was controlled by varying the irradiation times. A DC voltage source with a range from 0 to 30 V was used to carry out in-situ spectroscopic investigations of the composites prepared.

3.2 Experiments

As the color change in PDA is associated with conformational changes of PDA, understanding the transition dynamics requires real time monitoring of the same under stimulation. This is possible through in-situ spectroscopy, where typically PDA solutions are heated or made progressively more acidic/basic for investigations of thermochromism and solvatochromism, respectively. While the same principle applies to investigation of electrochromism, as CNT-PDA is in the solid state, the in-situ experiment set up has to be adequately modified to suit yarns/sheets as opposed to PDA

solutions. The following sections detail the steps taken to facilitate in-situ spectroscopic and other investigations used towards the completion of this thesis.

3.2.1 In-situ absorption spectroscopy

Absorption spectroscopy is typically carried out in solution. While solutions with dispersed PDA permit in-situ absorption studies for thermochromism and solvatochromism, it cannot be used for in-situ electrochromic investigations in PDA. This is because electrochromism requires the end to end alignment of CNTs to be maintained, unlike other PDA chromisms which are intrinsic to PDA. To facilitate in-situ absorption studies of electrochromism in CNT-PDA, a specimen stage was designed in-house using black, insulating card board, as shown in Figure 3.1. Accurate mounting of such a stage permits light from the spectrophotometer to pass through CNT-PDA in the solid state and also permits electrical connections to an external voltage source for in-situ experiments. All the absorption spectra in this research were obtained using a UV-2450 Spectrophotometer from Shimadzu Corp.

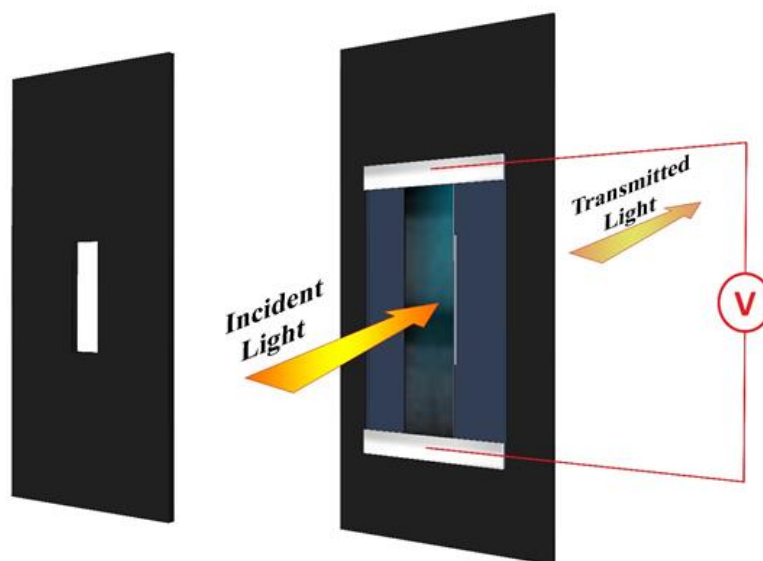


Figure 3.1 Insulating cardboard frame with window (left) and frame with CNT-PDA composite loaded and connected to an external voltage source (right).

3.2.2 In-situ Raman spectroscopy

The sample criteria for in-situ Raman investigations on electrochromism in CNT-PDA were far less rigid. As the typical sample holder is glass, it was straight forward to provide electrical connections to an external voltage source, without current shorting issues. The Raman shifts from PDA were observed using a source laser of 633 nm wavelength at a power as low as 0.05 %, using an inVia Raman microscope. The simplified setup for in-situ Raman measurements is shown in Figure 3.2.

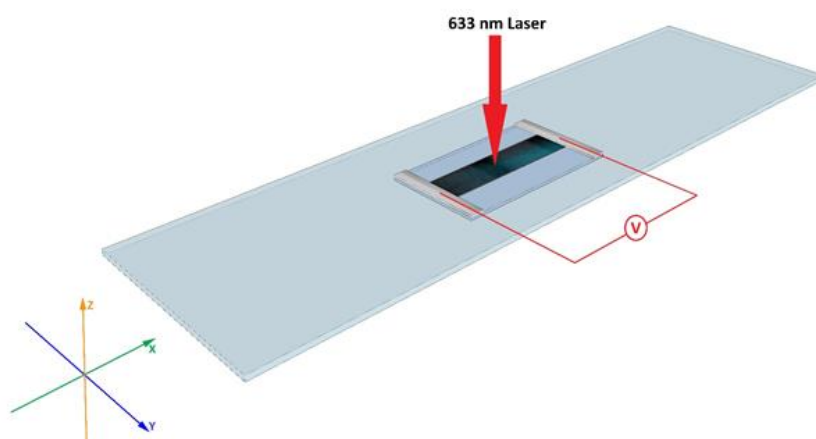


Figure 3.2 CNT-PDA composite mounted on glass slide and connected to voltage source for in-situ Raman studies.

3.2.3 Polarized Raman measurements

Unlike normal light, lasers are highly polarized, meaning that the wave vibrations occur along a single plane. This permits the prediction of alignment as favorably aligned materials will give forth a much stronger signal than others. Conveniently, the laser polarization is along the x-axis (the axis of alignment of CNTs in CNT-PDA composites) as shown in Figure 3.3. Hence, comparing the Raman intensities at various angles (0° to 90°) can give an estimate of the alignment of PDA with respect to CNTs. This method was used to verify current induced alignment changes in PDA in Chapter 5.

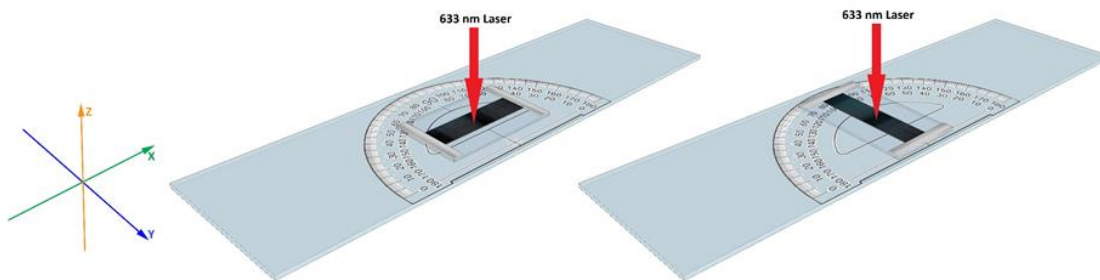


Figure 3.3 CNT-PDA composites oriented at 0° and 90° with respect to the laser polarization direction for polarized Raman studies.

3.2.4 Raman mapping

The Raman intensities over a pre-defined area can be used to form a map profile of the material surface. The software divides the area into tiny grids from which point spectra are obtained (Figure 3.4). The extremely low laser power (0.05 %) and short exposure time (1 sec for each point spectra) ensures that the laser induced surface effects are minimum. This is a significant advantage over conventional surface analysis techniques like SEM and AFM where the material surface is exposed to high energies for long durations for image acquisitions. In fact, accelerated e-beams can induce extended polymerization of PDA during the imaging process. Moreover, as the spectra

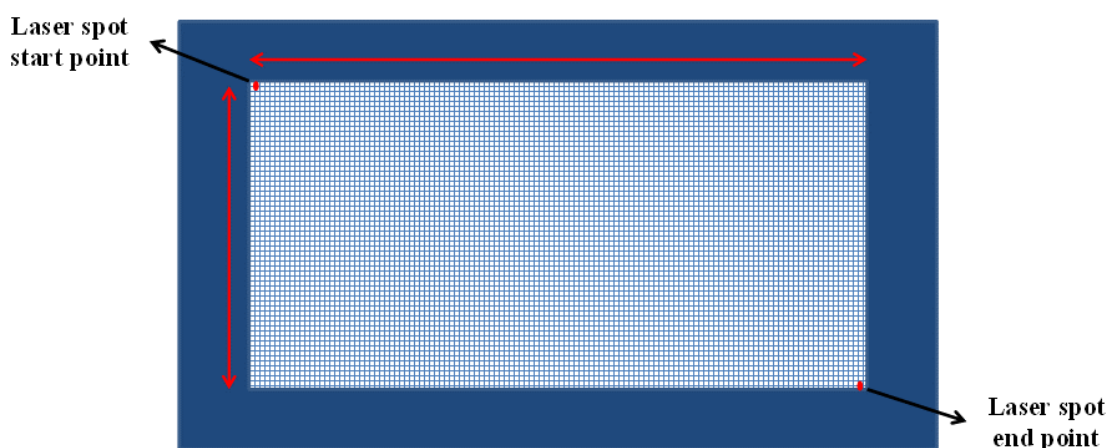


Figure 3.4 Schematic of the Raman mapping process. The blue section represents the surface of CNT-PDA composite. A spot Raman spectra will be obtained from each grid and the signal intensities mapped.

are obtained at ambient conditions, it is straight forward to provide electrical contacts to sample for map analysis before and after current flow.

3.3 Material characterization

Morphology of the as prepared composites was studied using field emission scanning electron microscopy (JEOL JSM-7600F). Surface roughness variations were estimated using Atomic Force Microscopy (AFM, Park Systems Co.). Diameters of individual MWCNTs were estimated using transmission electron microscopy (JEOL 2010, Japan). X-ray diffraction (PANalytical EMPYRIAN), the Netherlands) with a $\text{CuK}\alpha$ radiation source, at a scan rate of $0.013^\circ/\text{s}$ over a 2θ range of $3-30^\circ$ was used to determine monomer to polymer conversion of the composites. Kratos Axis Ultra, UK. Al $\text{K}\alpha$ (1486.6 eV) monochromatic X-ray source with emission of 10 mA and anode HT of 15 kV, calibrated to C 1s at 285 eV was used for XPS analysis.

Chapter 4 Growth of drawable CNT Forests and preparation of aligned CNT-PDA Composites

As explained in Chapter 1, this work is aimed at understanding the science behind electrochromic response of CNT-PDA composites. Polymerization of diacetylene monomers occurs only when the monomers are arranged in a specific organization (see section 2.3). This stringent requirement of monomer spacing can be met by using a host material which orients the monomeric units favorably prior to polymerization. In this work, CNT sheets act as the host material for the diacetylene monomers. These macroscopic forms of CNTs are obtained by a dry spinning process from arrays of vertically aligned CNTs prepared through chemical vapor deposition (CVD). The following sections of this report describe the steps for growth of CNT forests, assembly of CNT sheets from forests and the fabrication of CNT-PDA composites used in this work.

4.1 Growth of drawable CNT forests

In this work, growth of vertically aligned carbon nanotube (VACNT) arrays on Fe catalyst layer was realized using a Thermo Scientific thermal CVD reactor. A buffer layer of Al_2O_3 (thickness ~ 30 nm) followed by a thin film of Fe (thickness ~ 1 nm) was sputter deposited on to silicon wafers to form the catalyst substrates, similar to our previous reports [132, 133]. The as prepared catalysts were cut into pieces of adequate dimension so as to be inserted into quartz tubes for the Chemical Vapor Deposition (CVD) growth process.

The various stages involved in the carbon nanotube array (CNTA) growth process using CVD are shown in Figure 4.1. The prepared catalyst was ramped up to a sufficiently high temperature ~ 750 °C under a flow of carrier gas argon (Ar) and

reducing gas hydrogen (H_2). The catalyst was then subjected to annealing for ~ 7 minutes following which growth was

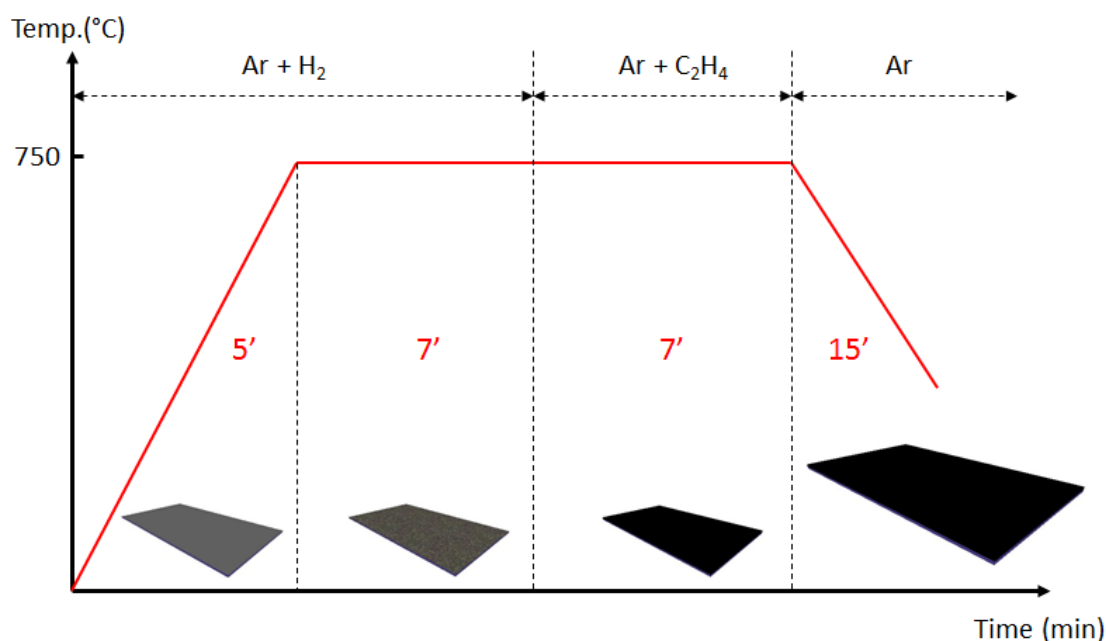


Figure 4.1 The various stages of CNT forest growth using thermal CVD. The times taken for each stage are shown in red.

initiated by introducing the carbon source (C_2H_4). Adequate pre-treatment of the catalyst is required to break up the catalyst film into uniform nanoparticles, which is crucial for uniform array growth. A very high pretreatment temperature could result in non-uniform cracking of the catalyst film and produce randomly sized particles. Such particles will not facilitate growth of uniform and drawable arrays.

In order to obtain high quality VACNT arrays, various parameters such as catalyst and buffer layer thickness, pretreatment temperature, feed gas flow rate, total gas pressure and growth time were optimized. These parameters differ with variations in experimental set up between different research groups. In general, VACNT arrays can be formed using catalyst layer thickness ~ 0.5 -3 nm at growth temperatures ranging from 600 – 900 °C. In this work, growth of VACNT arrays were carried out on catalysts with varying Fe and Al_2O_3 buffer layer thicknesses. Both the buffer layer and catalyst

metal layer was sputter deposited on the substrate silicon wafers with oxide thickness of 200 and 500 nm. Similar to other reported work, it was found that a thick buffer layer of alumina (~30 nm) below a relatively thin Fe layer (~1 nm) was essential for VACNT growth process.

The drawability ranking of CNT forests was made on a scale from 0 to 10 as indicated in Table 4.1. The overall gas flow rate through the quartz tube (~3 cm diameter and ~70cm in length) was maintained at 200 Sccm throughout the CVD process. The percentage of carbon in the source gas C₂H₄ was varied over a wide range to optimize drawability of the CNT forests. Figure 4.2a shows a two peak trend indicating growth of drawable forests for carbon percentages of ~21 and ~29, with the latter providing significantly better drawability. Subsequently, the CNT forests used for this study were prepared by maintaining carbon percentage ~29 during the growth process. The best conditions for growth were realized using the conditions listed in Table 4.2.

Table 4.1 Ranking criteria for CNT forests grown towards this research.

Rank	Criteria
10	Sheets can be spun continuously
9	Sheet length > 1 m, success rate high
8	Sheet length > 1 m, success rate low
7	Sheet length 50 – 100 cm
6	Sheet length 20 – 50 cm
5	Sheet length 10 – 20 cm
4	Sheet length 5 – 10 cm
3	Sheet length < 5 cm
2	Can draw out small ribbons
1	Not drawable, soft forests
0	Not drawable, hard forests

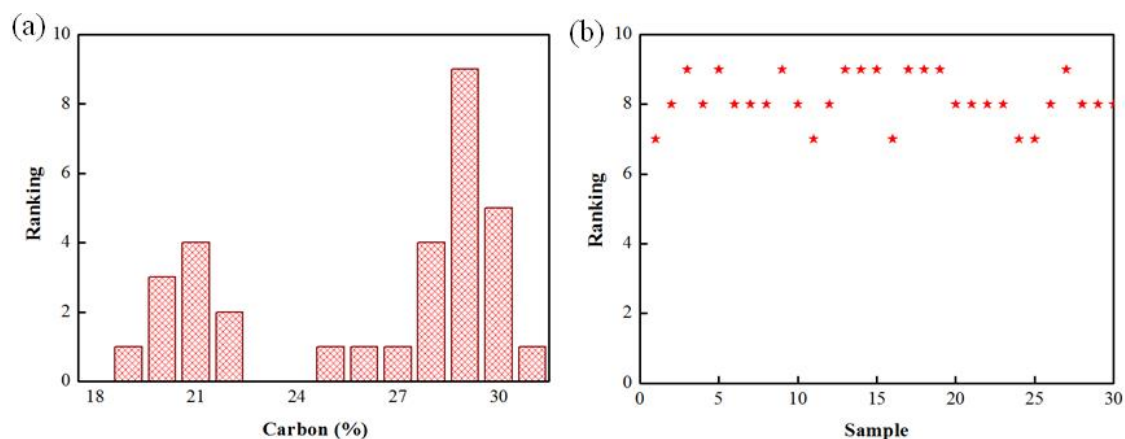


Figure 4.2 (a) Drawability ranking variation of CNT forests prepared with various carbon percentages during growth and (b) ranking variations between 30 samples grown using the optimized carbon percentage (29 %).

Table 4.2 The optimized growth parameters for drawable CNT forests.

Fe Thickness	Al ₂ O ₃ Thickness	Pretreatment	Growth	Carbon %
1 nm	30 nm	750°C, 7 mins	750 °C, 7 mins	29

4.2 Transferring CNT sheets from forests

A sharp blade was used to draw out a ribbon of CNTs from the edge of CNT forests prepared using the optimized growth conditions shown in Table 4.2. The width of the drawing tool determines the width of the CNT sheet. The process is schematically illustrated in Figure 4.3. A cylindrical sample loader was also used to ensure uniform transfer of multiple sheets on top of each other on 4 glass slides simultaneously, by controlling the number of rotations. For consistency, all the CNT sheets samples used in this research comprised of 5 layers, approximated to be 150 nm thick.

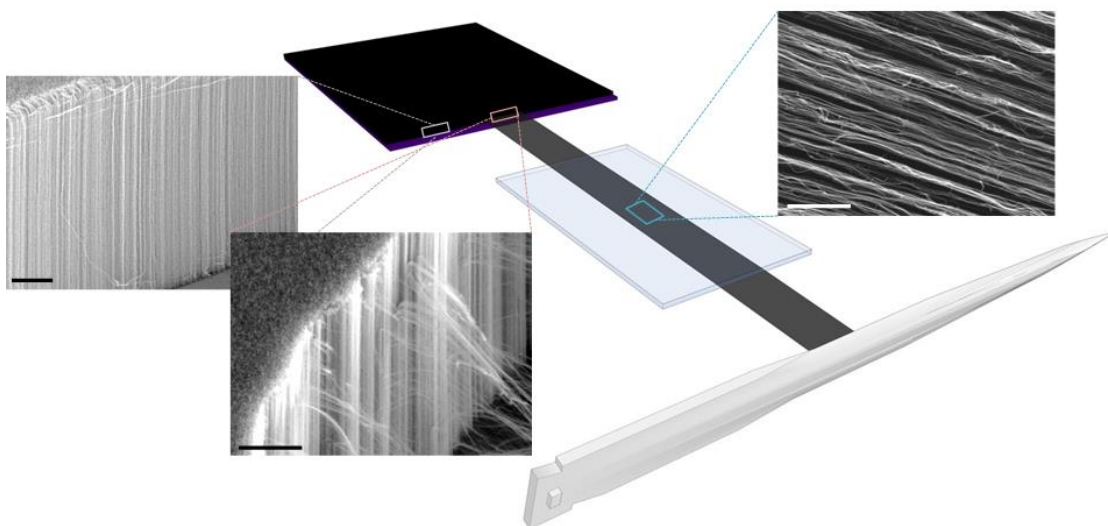


Figure 4.3 Schematic illustration of transferring CNT sheets from drawable forests on to glass slides. The magnified view of CNT alignment at various sections of the forests during the process are shown. The scale bar corresponds to 10 μm .

4.3 Preparing CNT-PDA composites

The DA precursor, 10,12-pentacosadiynoic acid (PCDA) was purchased from GFS chemicals. A solution of the monomer in tetrahydrofuran (THF) (10 mg/mL) was drop cast on to the CNT sheets on glass. For all the composites prepared in this work, it was ensured that only 20 μL of the DA solution was cast onto the sheets.

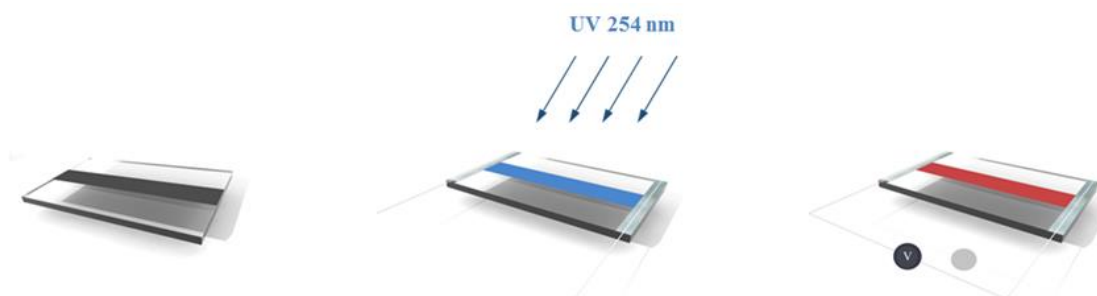


Figure 4.4 Schematic of the CNT-PDA composites fabrication process. Monomer incorporation (left) followed by UV irradiation (right) yields CNT-PDA composites. Silver paint was used to provide electrical contacts. Current flow through CNT-PDA causes color change to red (right).

The DA incorporated sheets were dried in air and subjected to UV-254 nm irradiation. The extent of polymerization was controlled by regulating the exposure time of the DA incorporated sheets to UV light. Post polymerizations, the samples were provided with electrical contact using conducting silver paint (and metal wires in some cases). The process is schematically illustrated in Figure 4.4.

4.4 Controlling extent of polymerization of DA

Typical techniques to determine extent of polymerization of a monomer requires the polymer to be dissolved in a good solvent. Unfortunately, PDA is notoriously difficult to dissolve. Moreover, a suspension of scraped PDA film in THF appeared red in color; measuring extent of polymerization from such a suspension will not give an accurate estimate of polymerization in the blue CNT-PDA composite films prepared as described in section 4.3. Hence, alternative modes to estimate degree of polymerization in CNT-PDA composites had to be explored.

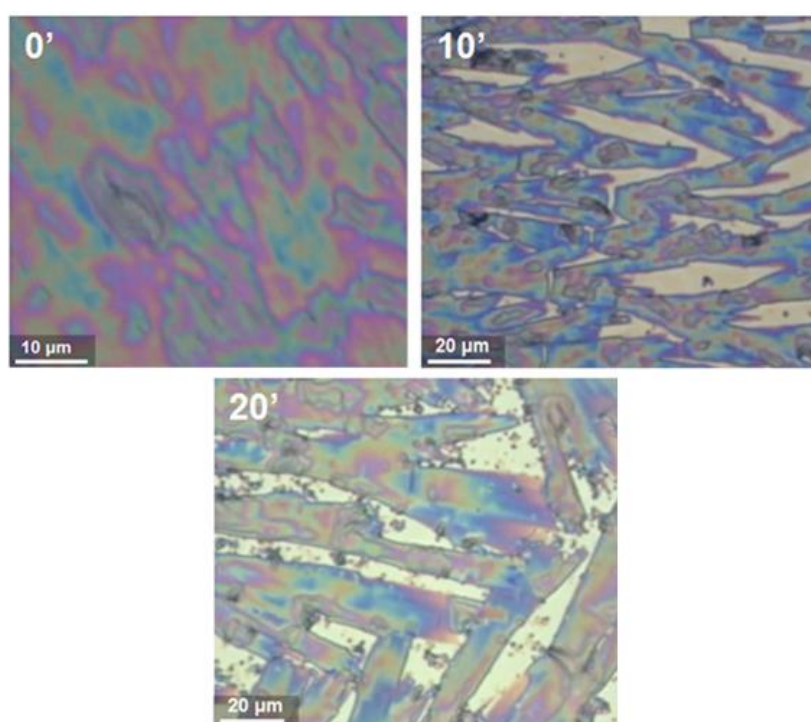


Figure 4.5 Evolution of crystalline PDA domains upon exposure of DA cast on silicon wafer to UV-254 nm irradiation for different times (0, 10 and 20 mins).

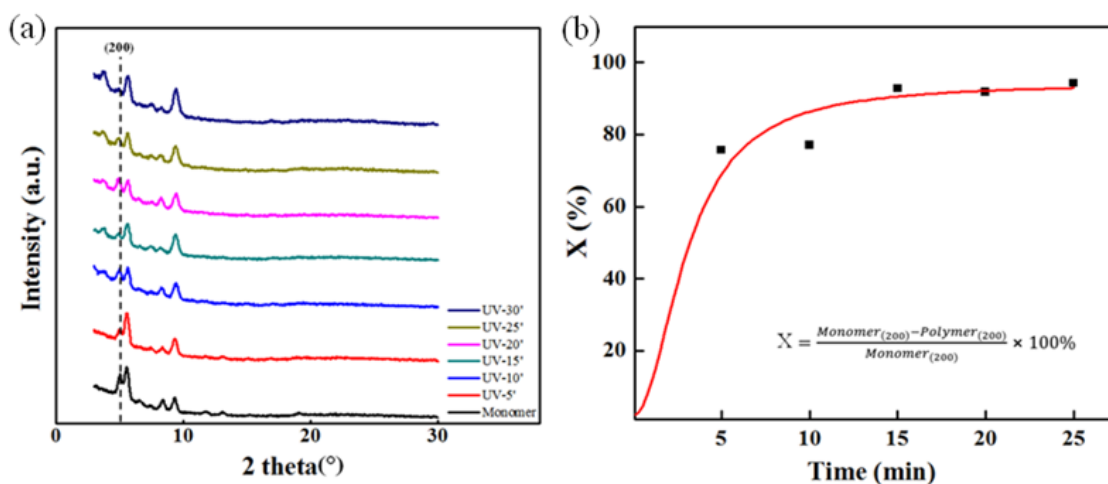


Figure 4.6 (a) XRD profiles of PDA on Silicon obtained after different UV exposure times and (b) percent conversion of DA with UV treatment time based on (200) Bragg peak.

We cast 10,12-PCDA onto silicon wafer, dried the samples in air and subjected the monomer films to UV-254 nm irradiation for different durations. From subsequent optical microscope images, we noticed that UV exposure resulted in small crystalline domains that increased in length and thickness with increasing exposure times (Figure 4.5). Although the increasing domain sizes provide some evidence for the extent of DA polymerization, a quantitative estimate requires further information on the structural changes induced in the DA film.

To this end, Shufang et al. [87] used XRD to probe the structural differences originating with increasing UV exposure times in PDA films and found that the area percentage of the diffraction peaks could be used to accurately predict the percentage of polymer content in the films. XRD profiles of DA on silicon subjected to increasing UV exposure times typically had 5 Bragg's peaks as shown in Figure 4.6a. A plot of the percentage monomer conversion as a function of UV exposure time obtained using the (200) peaks, curve-fitted with the in-built Hill1 function in Origin, confirmed that polymerization proceeds rapidly with up to 80 % conversion in 5 minutes of UV

exposure (Figure 4.6b). Unless stated otherwise, CNT-PDA composites used in this work were prepared with 10 minutes of UV-254 nm exposure.

Chapter 5 A study of electrochromism in CNT-PDA composites

5.1 Introduction

Horizontally aligned carbon nanotube (CNT) sheets and fibers drawn from vertically aligned CNT forests are the closest we have reached in terms of replicating the impressive properties of individual CNTs in a macroscopic form factor [59, 88]. Not only are these structures mechanically strong, highly conducting and flexible, they are also ideal templates to form multifunctional hybrids through surface functionalization, which make them attractive for a broad range of applications [89-96].

Of the various conjugated polymers that can be non-covalently adhered onto the surface of MWCNT sheets and fibers, PDA has the unique intrinsic ability to respond to different stimuli such as light, heat, mechanical force, change in pH and foreign molecules with a distinct color change from blue to red [40, 97-110]. Detailed investigations of PDA in the solid state, organic solvents and aqueous solutions have shown that the PDA backbone and side chain geometries are contributing factors to the color exhibited by PDA [8, 39, 105, 111-113]. Ordinarily, PDA formed from the diacetylene (DA) monomer 10,12-pentacosadiynoic acid (PCDA) does not exhibit reversible chromatic transitions [114]. However, by polymerizing 10,12-PCDA on the surface of multi-walled carbon nanotube (MWCNT) fiber, Peng et al. [9] successfully demonstrated a reversible electrochromic transition between the blue and red phase of PDA on the MWCNT surface, for up to 14 cycles of current.

Hence, not only was the transition reversible, it was also induced electrically, which significantly broadened the scope for practical applications of these composites. Interactions between the polymer and MWCNT enabled by three-dimensional electron

hopping conduction, resulting in reduced delocalization of π -electrons along the PDA chains, was proposed as a likely mechanism for electrochromism in these composites. This assumption was based on already established mechanisms for thermochromism and solvatochromism of PDA, wherein the blue phase has extended conjugation which gets disrupted under stimulus, to yield the red phase [115, 116]. However, reversible chromism in PDA is typically attributed to strong H-bond interactions between neighboring head groups and a lot of effort has been put into engineering DA monomers with tailored groups, capable of enhanced H-bonding interactions. As there is no possibility of strong H-bond interactions in the PDA resulting from 10,12-PCDA, it stands to reason that electrochromism in MWCNT-PDA composites occurs through a different route. The MWCNT-PDA composites used in this work were prepared as illustrated in Figure 5.1 and explained in more detail in section 4.4. The photographs of the composites at various stages of preparation are shown in Figure 5.2.

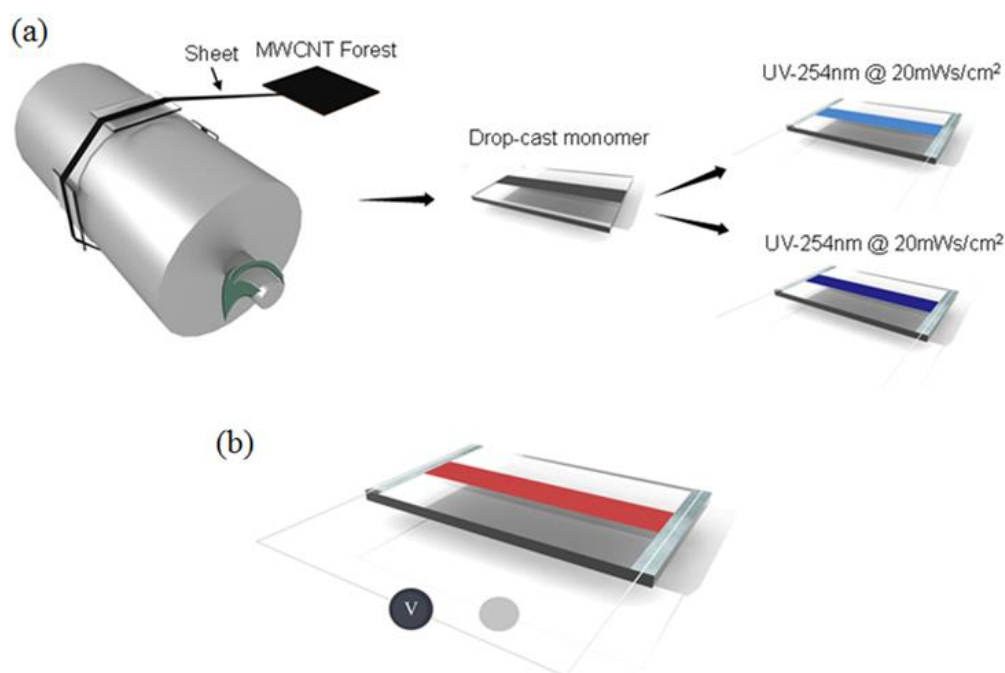


Figure 5.1. (a) Schematic illustration of MWCNT-PDA fabrication and (b) the electrochromic blue to red transition.

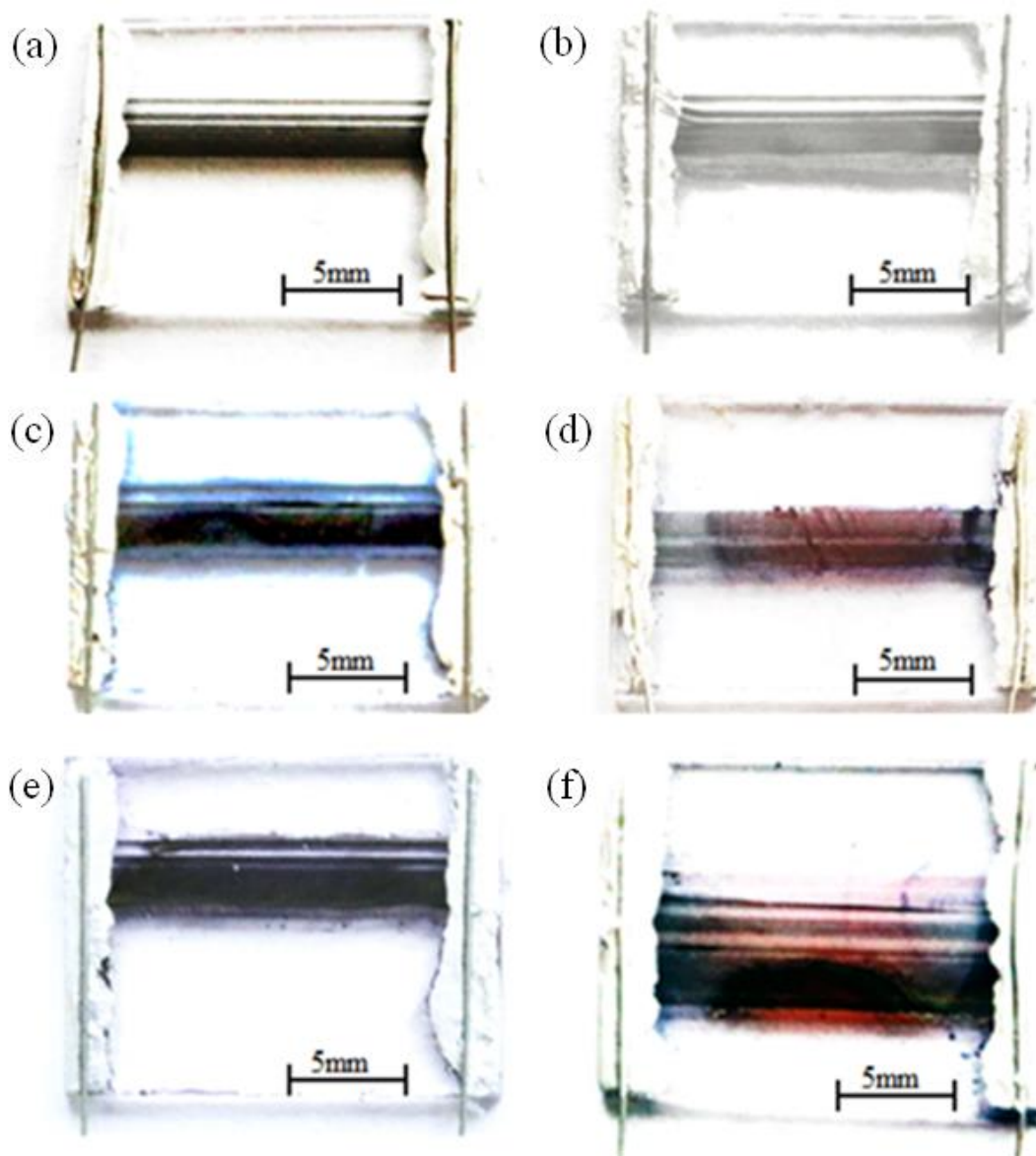


Figure 5.2 (a) Digital photograph of typical device with pristine MWCNT sheets transferred to glass slide, (b) monomer incorporated MWCNT sheet, (c) partially polymerized MWCNT-PDA composite, (d) electrically induced red phase of the partially polymerized composite and (e) the blue and (f) red phase of the highly polymerized composite.

5.2 Current induced morphology changes

The high degree of alignment in the untreated MWNT sheets can be seen in the scanning electron micrograph shown in Figure 5.3a. After incorporation of DA monomer followed by evaporation, a uniform surface coating resulted (Figure 5.3b).

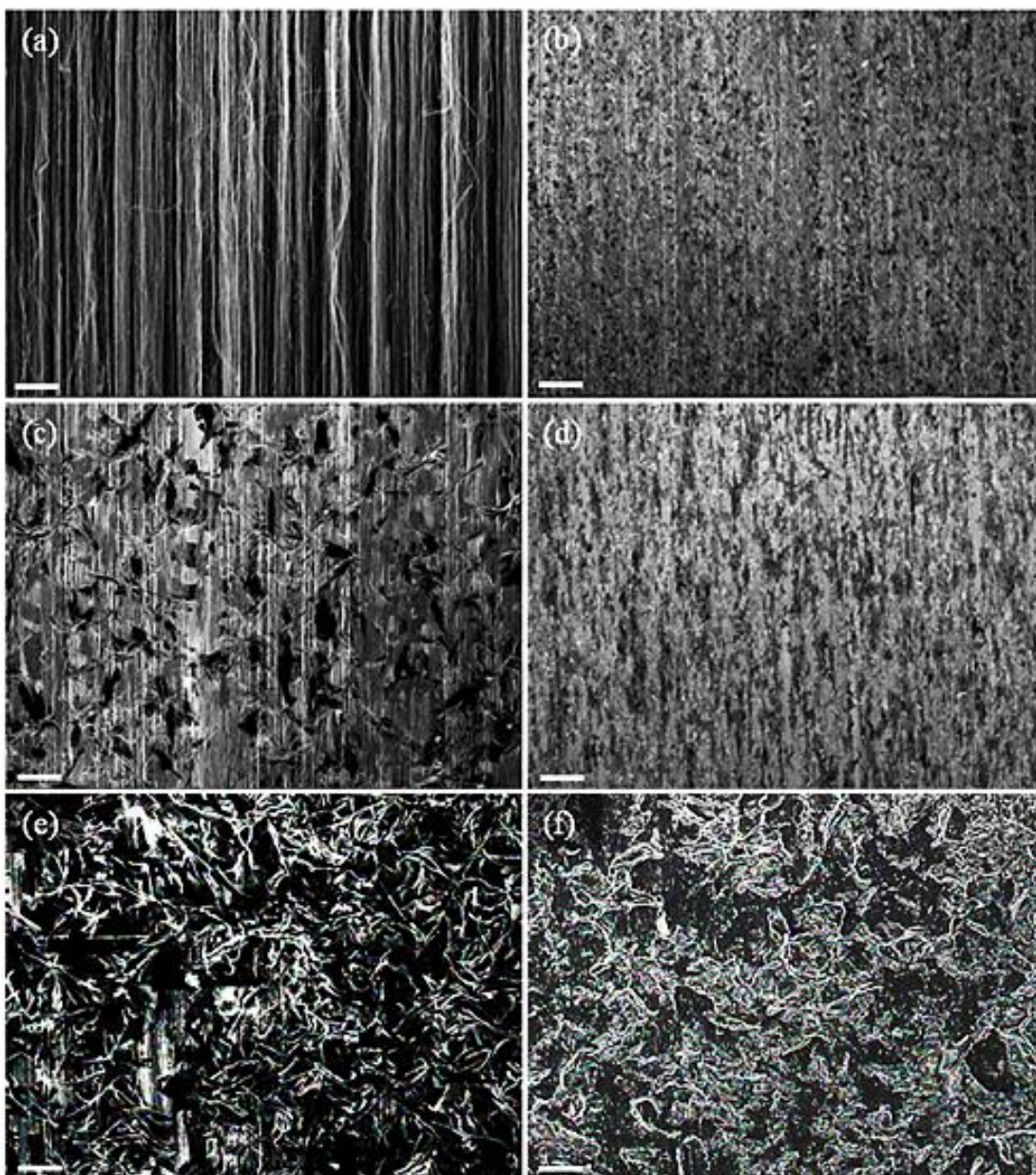


Figure 5.3 (a) FESEM morphology of pure MWNT sheet, (b) DA incorporated sheet, (c) partially polymerized composite, (d) partially polymerized composite after current flow, (e) highly polymerized composite and (f) highly polymerized composite after current flow. The scale bars correspond to 10 μm .

Polymerization with UV-254 nm light at a dose of 20 mWs/cm² resulted in the formation of distinct polymerized domains along the surface of MWCNTs (Figure 5.3c).

The percent monomer conversion at the UV irradiation dose of 20 mWs/cm² was estimated to be about 15 % from the XRD data, which suggested only partial polymerization of DA occurred [87]. These partially polymerized composites typically

appeared light blue in color. Figure 5.3d shows the morphology of the electrically induced red phase of the same composite, where polymer morphology showed obvious differences. DA incorporated MWCNT sheets subjected to a UV irradiation dose of 250 mWs/cm², accounting for around 90% conversion of the monomer, revealed large PDA segments covering major portions of the underlying MWCNTs (Figure 5.3e).

Though the overall polymer growth did not appear to follow a specific pattern, we could observe that the PDA in the blue phase oriented largely along a plane perpendicular to that of the MWCNTs. Interestingly, the corresponding red phases (Figure 5.3d and f) revealed different features, indicating reordering of the polymer along the underlying MWCNTs.

These observations were supported by AFM studies of partially and highly polymerized MWCNT-PDA composites, before and after passing current (Figure 5.4). The surface roughness (Ra) values of the red phases of both partially and highly polym-

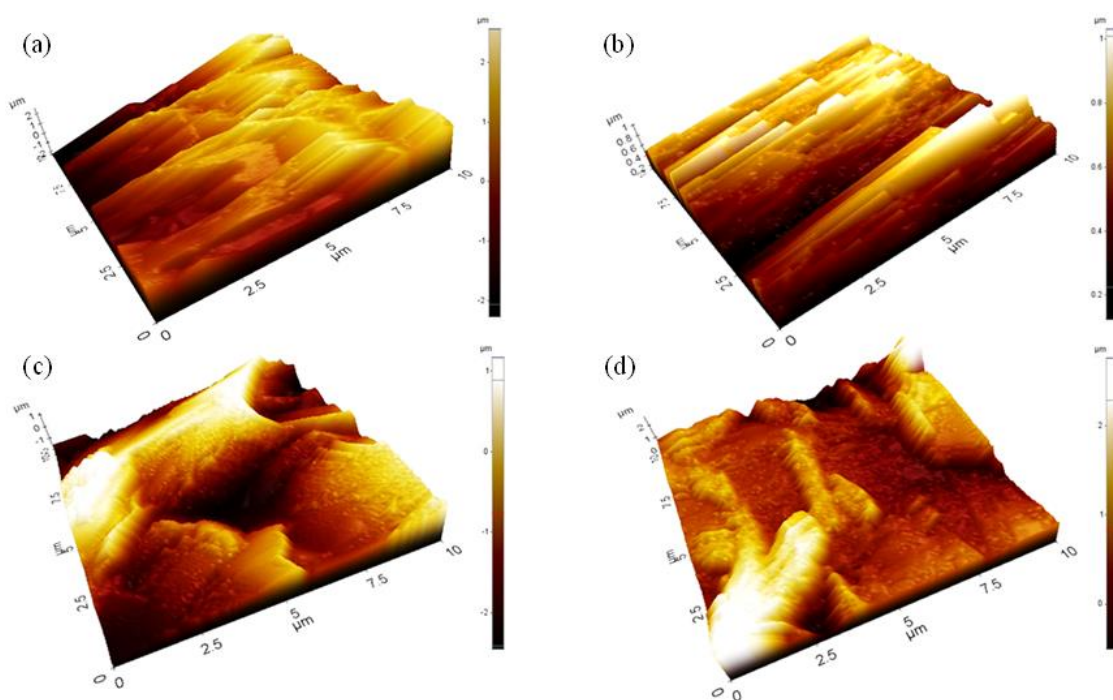


Figure 5.4 (a) AFM surface profiles of partially polymerized blue phase (before current) and (b) red phase (after current). (c) and (d) show the profiles of blue (before current) and red phases (after current) of highly polymerized composites.

-erized composites were significantly lower than their blue phases: 0.13 and 0.22 μm for the red phases as opposed to 0.78 and 0.67 μm for the blue phases, respectively. It was thus evident that current flow can cause significant changes in morphology and surface profiles of both partially as well as highly polymerized MWCNT-PDA composites.

5.3 The blue to red phase transition

The electrically induced change in absorption of the MWCNT-PDA composites in the visible range (400-700 nm) was monitored by recording the absorption spectrum while current flowed through the composites. As expected, in the absence of stimulus, the composites appeared blue with absorption maxima at 650 nm and an accompanying vibronic peak close to 590 nm (Figure 5.5).

A similar spectroscopic investigation of solvatochromism of PDA vesicles revealed a blue to red transition through an 'isosbestic' point, which refers to a particular wavelength where absorption due to the blue and red phases are the same, throughout the transition [115]. In-situ thermochromic response of PDA vesicles were also characterized by an isosbestic point at about 565 nm [117]. The presence of an isosbestic point in the spectral transition is indicative of a direct conversion from the blue to red phase, without formation of intermediate states, typically associated with irreversible chromism in PDAs [114]. As there are no isosbestic points in the in-situ absorption spectra of either type of MWCNT-PDA composites used in this study, it stands to reason that the electrochromic transition is not a straightforward quantitative conversion of the blue to red phase but rather, involves at least one intermediate phase. Moreover, gradual shifts in absorption in response to stimulus are typically expected only from PDAs with strong head-group interactions through H-bonds. As mentioned previously, PDA formed from 10,12-PCDA do not have head groups capable of strong

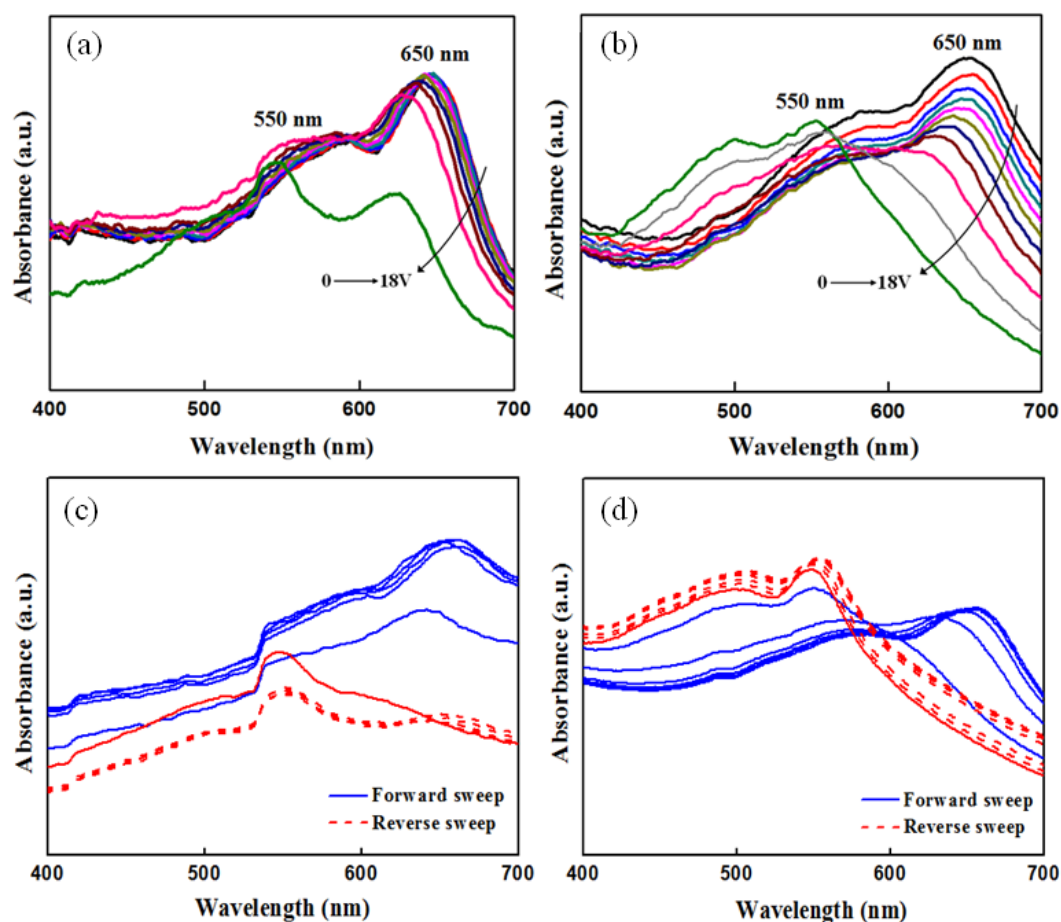


Figure 5.5 (a) In-situ variation in absorbance spectra with voltage of partially polymerized and (b) highly polymerized MWNT-PDA composites; (c) corresponding spectra under forward and reverse bias for partially and (d) highly polymerized composites.

H-bond interactions with neighboring side chains [8, 114]. This observation suggests that the PDA head groups and side chains may not have a significant role in the electrochromic transition unlike solvatochromism and thermochromism.

5.4 Stress in the PDA backbone

Double and triple bonds of carbon give well defined Raman peaks at 1450 and 2080 cm^{-1} , respectively [116]. The backbone of PDA is composed entirely of alternating single, double and triple bonds of carbon and hence Raman spectroscopy is ideal to study changes that occur along the PDA backbone. Raman studies on PDAs have

revealed significant red shifts of both $\nu_{C=C}$ and $\nu_{C\equiv C}$ in the thermally induced red phase [116, 118]. It was thus natural to expect similar red shifts in the electrically induced red phase of the MWCNT-PDA composites used in this work.

The laser excitation wavelength of 633 nm was chosen as it lay within the band gap of PDA. For pure MWCNTs, the distinct peaks at 1345, 1580 and 2700 cm^{-1} correspond to D, G and 2D bands, respectively. Due to the superficial coating of the monomers on the surface of MWCNTs as well as the low excitation laser power used, we do not observe traces of these bands in the spectra of the composites. The major difference between monomer coated and polymerized composites was the increased intensity corresponding to $\nu_{C\equiv C}$, which is direct evidence for the onset of polymerization as the contribution due to conjugated bonds are expected to increase when monomers align to form conjugated PDA chains.

In order to understand the changes in the PDA backbone as a result of current flow through underlying MWCNTs, in-situ Raman spectra were obtained with voltage increments of 2 V, up to 18 V. The corresponding spectra of the partially and highly polymerized MWCNT-PDA composites in the region relevant to PDA backbone are shown in Figure 5.6. For the partially polymerized composites, the peak positions and

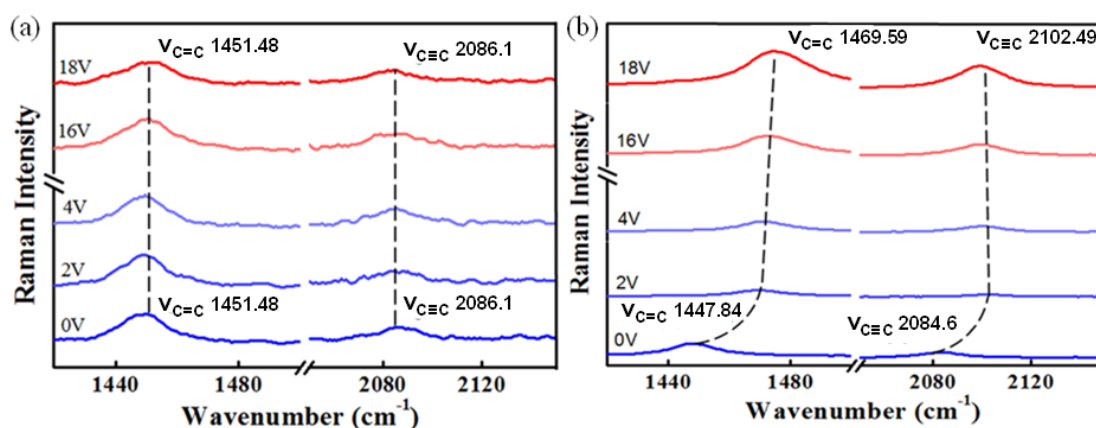


Figure 5.6 (a) In-situ Raman spectral shifts in the region pertaining to PDA backbone of partially polymerized and (b) highly polymerized composites.

intensities remained more or less the same at all applied voltages, as indicated by the dashed lines in Figure 5.6a. But we know from the in-situ absorption spectral transition that a blue to red transition occurred at about 14 V (Figure 5.5a). Hence, the color change does not alter the Raman peaks of $\nu_{C=C}$ and $\nu_{C\equiv C}$ in partially polymerized composites. It is inconsistent with previous Raman studies of PDA in which the blue phase exhibits $\nu_{C=C}$ and $\nu_{C\equiv C}$ at 1455 and 2083 cm^{-1} with the corresponding red phase having red-shifted $\nu_{C=C}$ and $\nu_{C\equiv C}$ at 1516 and 2118 cm^{-1} , respectively [116]. In our case, passing current through partially polymerized MWCNT-PDA composites yielded a red phase with $\nu_{C=C}$ and $\nu_{C\equiv C}$ at 1451.48 and 2086.1 cm^{-1} respectively, which is typically expected for blue PDA. As the absence of Raman shifts rule out stress generation in the backbone, it is very likely that stress in the backbone is not crucial for formation of red phase in PDAs.

A similar analysis of the peaks due to $\nu_{C=C}$ and $\nu_{C\equiv C}$ in the highly polymerized samples revealed significantly different results (Figure 5.6b). In the absence of electrical stimulus, $\nu_{C=C}$ and $\nu_{C\equiv C}$ occurred at 1447.84 and 2084.6 cm^{-1} , respectively. Application of a potential caused red shifts of these peaks. Raman shifts are drastic at low voltages with maximum shifts of 21.75 and 17.85 cm^{-1} for $\nu_{C=C}$ and $\nu_{C\equiv C}$ peaks respectively at a potential as low as 2 V, beyond which the change is very mild, as indicated by the dash lines in the Figure 5.6b. These shifts are expected for the red phase of PDAs which is typically obtained by subjecting the blue phase to stimuli such as heat, mechanical stress and solvents.

Stress in the backbone is believed to cause red-shifts of Raman peaks and hence the red phase is understood to have a more stressed backbone structure [10, 103]. However, it is unlikely that stress in the backbone causes the formation of red phase in PDAs because Raman shifts have not been observed in our red phased partially polymerized samples. If stress in the backbone was the primary factor influencing color

change, we should expect similar responses both in partially polymerized and highly polymerized composites. Hence, we tentatively conclude that stress in the red phased highly polymerized composites is a consequence and not necessarily the cause of the color change.

5.5 Evidence for PDA realignment

Raman spectra recorded at different orientations with respect to the polarization direction of the incident laser beam has been demonstrated to be a useful technique to estimate degree of alignment in composite samples with dispersed CNTs [119, 120]. We obtained Raman spectra at 0°, 30°, 60° and 90° with respect to the MWCNT sheet axis for the blue and red phases of partially and highly polymerized samples. The intensity of the most prominent $\nu_{C=C}$ peak ($\sim 1450\text{ cm}^{-1}$) was compared in all cases to get an idea of the alignment of PDA chains in the two phases.

For the partially polymerized composites, the blue phase gave forth a much stronger signal when the sample was aligned at 90° as opposed to 0° (Figure 5.7a), suggesting that more of the PDA backbones were aligned against the axis of MWCNT sheets, to bridge MWCNTs. In its corresponding electrically induced red phase, the trend was reversed, with $I(\nu_{C=C})$ at 0° significantly higher than $I(\nu_{C=C})$ at 90° (Figure 5.7b).

Polarized Raman on MWCNT-PDA composites with an intermediate monomer conversion $\sim 50\%$ also suggested a significant realignment of PDA chains along the MWCNT axis in the red phase, akin to the case of partially polymerized composites (Figure 5.7c and d). For highly polymerized composites, $I(\nu_{C=C})$ at 0° was higher than $I(\nu_{C=C})$ at 90° in the blue as well as the red phase, however, Raman shifts were evident in the red phase (Figure 5.7e and f).

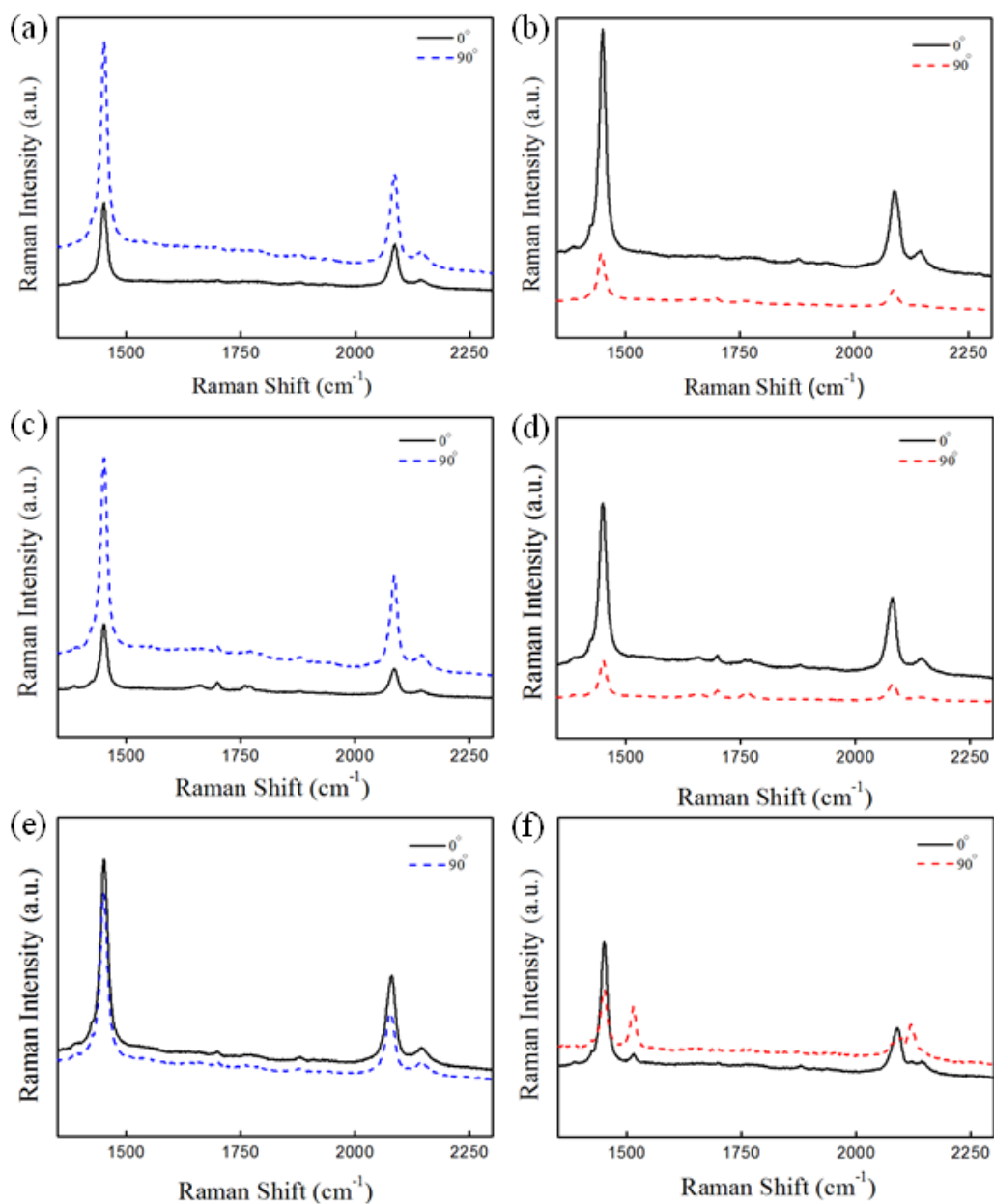


Figure 5.7 (a) Raman spectra obtained at 0° and 90° configurations with respect to incident laser polarization direction for partially polymerized blue phase and (b) the corresponding electrically induced red phase, (c) intermediately polymerized blue phase and (d) corresponding electrically induced red phase, (e) highly polymerized blue phase and (f) the corresponding red phase.

In order to validate change in alignment from the blue to the electrically induced red phase, the variation of intensity ratio $v_{C=C}(\alpha^\circ)/v_{C=C}(0^\circ)$, (where α denotes the sample offset angle), as a function of α was studied (Figure 5.8). It was found that for the partially polymerized samples, the blue phase showed a steady increase in $v_{C=C}(\alpha^\circ)/$

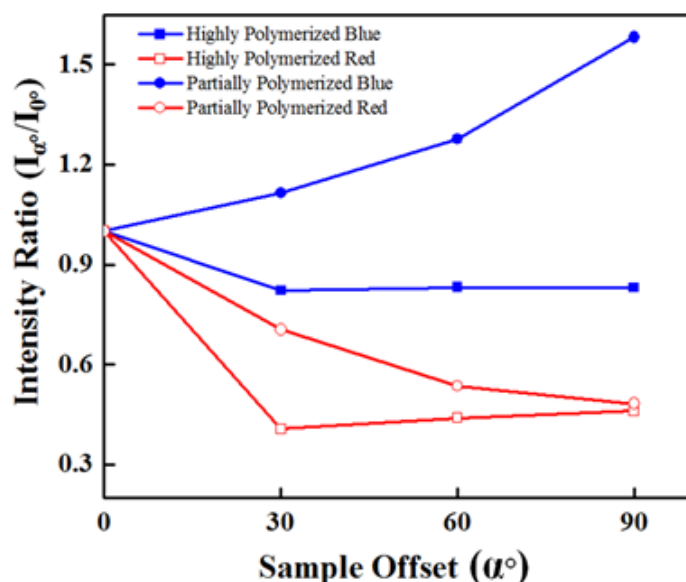


Figure 5.8 Raman intensity ratios (I_α/I_0) of MWCNT-PDA composites as a function of the angle (α) between the fiber axis and the incident laser polarization axis.

$v_{C=C}(0^\circ)$, with increasing α . On the other hand, the electrically induced red phase showed an opposite trend with $v_{C=C}(\alpha^\circ)/v_{C=C}(0^\circ)$ decreasing with increasing α .

Prior to current flow, it was estimated that the number ratio of PDA backbones aligned along the MWCNTs over those aligned against MWCNTs (I_0/I_{90°) was 0.63. After current flow, this ratio increased to 2.07, indicating more PDA backbones aligned along MWCNTs. For highly polymerized composites, both the blue and red phases revealed similar general trends where $v_{C=C}(\alpha^\circ)/v_{C=C}(0^\circ)$ reduced with increase in α . In this case, current flow caused a less drastic change in the ratio from 1.2 to 2.1. Hence current flow facilitates reordering of PDA backbones along the MWCNT axis.

5.6 Mechanistic Interpretation

Even though PDA is a poor conductor compared to MWCNT, current flowing through underlying MWCNTs in MWCNT-PDA composites can be expected to influence PDA. This stems from the fact that current flow through macroscopic

assemblies of MWCNTs drawn from MWCNT forests occurs via three-dimensional electron hopping between neighboring bundles, increasing the odds of electron interaction with PDA [61]. The in-situ spectroscopic studies carried out on the MWCNT-PDA composites clearly showed the formation of red phase in PDA with characteristic $\nu_{C=C}$ and $\nu_{C\equiv C}$ at 1451.48 and 2086.1 cm^{-1} for partially polymerized and 1469.59 and 2102.45 cm^{-1} for highly polymerized composites, respectively. The absence of Raman shifts from the blue to red phase transition under electrical stimulus for the partially polymerized composites suggests that factors other than backbone stress and side chain strains contribute towards the color exhibited by PDA. A possible explanation for this could be inferred from the work on stacked bi-layers of graphene nano ribbons (GNR) carried out by Zhong et al. [121]. GNRs stacked in perfect alignment were shown to have significantly improved transport properties as well as a drastically reduced band gap as opposed to misaligned stacks and monolayers of GNRs. These improvements were attributed mainly to the interlayer interactions of delocalized π -electrons, which inevitably become significant when the π -orbitals stack perfectly.

Based on the morphological differences, in-situ absorption and Raman spectral changes with voltage, we propose the following mechanism for blue to red color transition in MWCNT-PDA composites under electrical stimulus. UV irradiation initiates polymerization of the DA monomers on the surface of MWCNTs. Under low UV dose, very small polymerized regions are formed with PDA backbones oriented in different directions, with a slight preference for alignment against MWCNT axis (Figure 5.9a). Applying a voltage across these MWCNT-PDA composites initiates three dimensional hopping of electrons along and across MWCNT bundles. Consequently, the flexible backbones of PDA realign to favor efficient π - π interactions between the sp^2

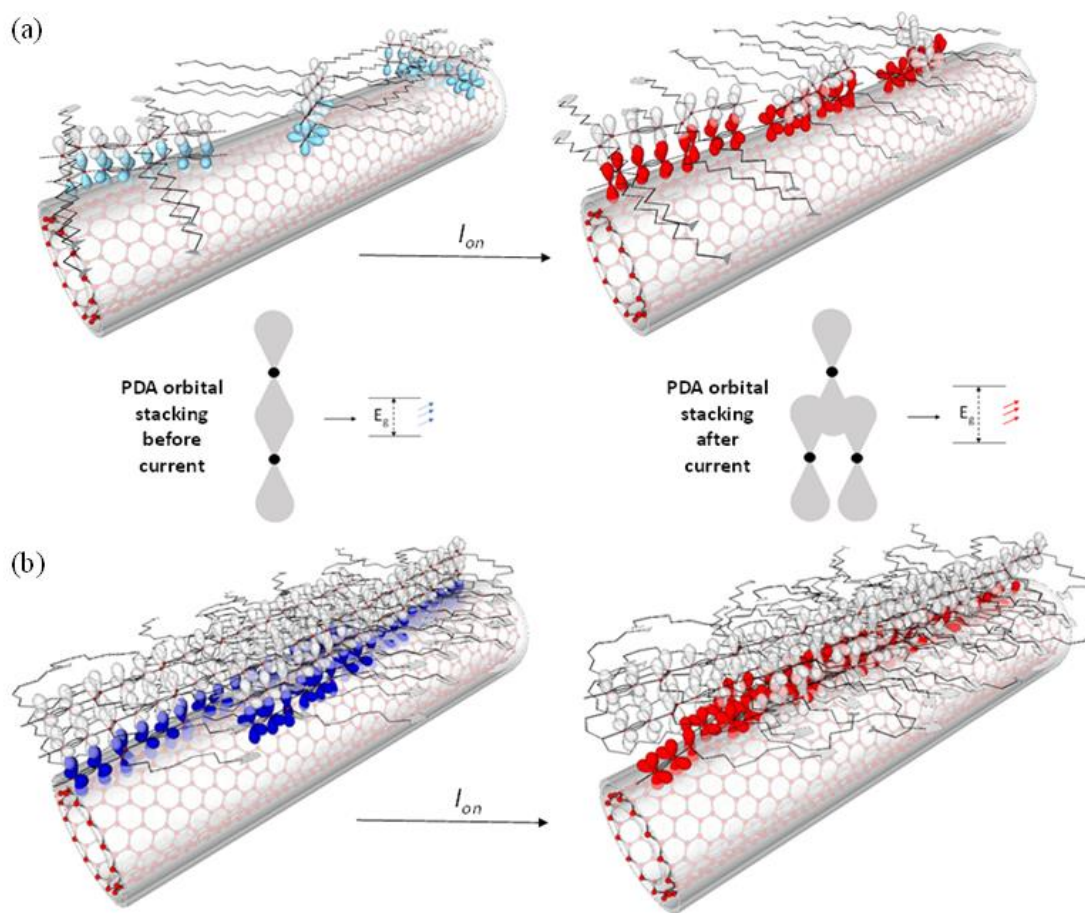


Figure 5.9 (a) Proposed mechanism for electrochromism in partially polymerized and (b) highly polymerized MWCNT-PDA composites.

hybridized orbitals at the MWCNT-PDA interface. The short PDA backbones in immediate proximity of MWCNT have no difficulty in changing alignment with little or no interaction with neighboring PDA backbones and side chains, explaining the lack of stress induced shifts in the Raman spectra of partially polymerized composites (Figure 5.6a). PDA further away from the MWCNT surface are not influenced significantly by current flow and do not change alignment as drastically as the PDA layers closer to the PDA-MWCNT interface. This results in de-stacking of PDA orbitals. An accompanying widening of band gap analogous to the case of de-stacked GNRs reported by Zhong et al. [121] causes the drastic color shift to red in these partially polymerized MWCNT-PDA composites.

Higher UV dosage results in much longer PDA chains in close proximity (Figure 5.9b). While the underlying principle is the same for highly polymerized MWCNT-PDA composites, the significantly longer backbones and accompanying side chains inevitably face difficulty in aligning favorably for efficient π - π interactions at the MWCNT-PDA interface due to inter backbone-backbone and backbone-side chain interactions. This explains why there are stress induced Raman shifts of $\nu_{C=C}$ and $\nu_{C\equiv C}$ in highly polymerized MWCNT-PDA composites when subjected to electric current (Figure 5.6b). Prior to current flow in the partially polymerized composite, short PDA backbones prefer alignment against MWCNT axis. Current flow causes realignment of PDA along the MWCNT direction. Thus, current induced change in alignment results in de-stacking of PDA orbitals. De-stacking widens the bandgap of PDA, triggering the visible color change of the composites to red. Short PDA chains in the partially polymerized composites undergo realignment with little interaction with neighboring chains, eliminating stress generation; realignment of longer PDA chains in the highly polymerized composites results in physical interactions with neighboring PDA chains which hinders movement, causing a stressed structure.

Scanning tunneling microscopy (STM) and a resulting estimate of the band-gap of partially and highly polymerized CNT-PDA obtained before and after current flow can validate this mechanism, which is proposed based on the results of in-situ Raman, absorption spectroscopy and polarized Raman experiments. Electrochromism invoked by MWCNTs combined with the intrinsic chromatic response of PDA to heat, mechanical force and chemicals, make MWCNT-PDA composites attractive for diverse applications.

5.7 Versatility of CNT-PDA chromism

Though electrochromism in CNT-PDA is the most exciting chromatic response yet, the best scenario would be to have a material which responds to a wide range of stimuli. As previously mentioned, PDA is capable of intrinsic chromatic transitions to various stimuli such as heat, force and chemicals. If incorporation of CNTs to realize electrochromism in CNT-PDA drastically hampers other inherent chromatic responses of PDA, the resulting hybrid may not be as versatile as expected. We thus carried out experiments to verify if CNT-PDA composites do indeed respond to chemicals and thermal stimulus, as expected for pure PDA. The results (illustrated in Figure 5.10) confirm that CNTs do not hinder the intrinsic chromatic response in PDA. In fact, the thermochromism of CNT-PDA seemed to be rather sensitive to temperature with a distinct color change to red visible only beyond 80° C. The transitions were also irreversible, as expected for PDA from 10,12-PCDA.

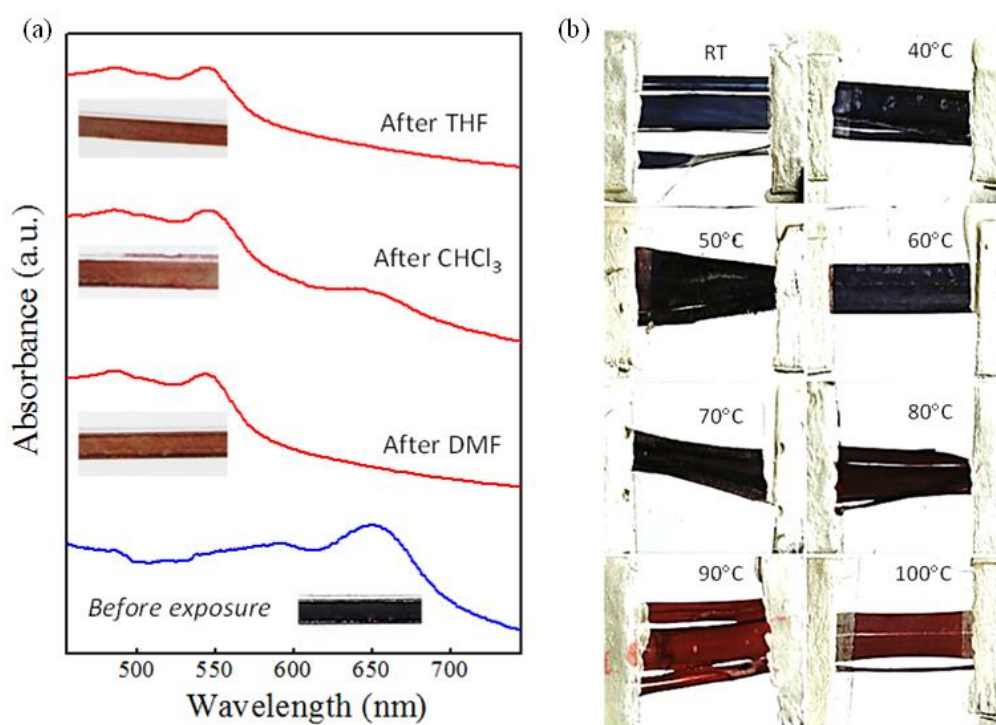


Figure 5.10 (a) The chromatic response of CNT-PDA composites to different chemicals and (b) temperature.

5.8 Summary

We investigated the mechanism of electrically induced blue-to-red transitions in partially and highly polymerized MWCNT-PDA composites via in-situ Absorption and Raman spectroscopy. The evolution of absorbance with voltage revealed a clear transition from the blue to red phase in both class of composites. However, composites formed by higher dose of UV irradiation showed significant red shifts in the Raman spectra with increasing voltage as opposed to the partially polymerized composites. By linking the spectroscopic results with morphological variations and polarized Raman analysis before and after passing current, we proposed a mechanism whereby current flow induces de-stacking of π -orbitals in PDA, widening the band gap of PDA and thus changing color to red. Significant inter chain backbone-backbone and backbone-side chain interactions in the highly polymerized composites gave rise to stress based Raman shifts of $\nu_{C=C}$ and $\nu_{C\equiv C}$ by 21.75 and 17.85 cm^{-1} , respectively. Much shorter PDA chains in the partially polymerized composites realigned without the introduction of stress as inter chain backbone and side chain interactions were minimum. Hence, it was found that a stressed PDA backbone was not a pre-requisite for red phase formation under electrical stimulus in MWCNT-PDA composites.

Chapter 6 Dependence of critical transition voltage on interaction between CNT and PDA

6.1 Introduction

Diacetylene monomers under favorable orientation undergo rapid solid state polymerization upon UV irradiation to yield blue polydiacetylene (PDA). This blue phase, when subjected to stimuli such as heat, mechanical force and foreign molecules, switch to a red phase [97-99, 102, 103, 105, 108, 110]. Typically, the blue to red transition in PDA is irreversible. However, as explained in section 2.12, PDA when combined with dry spun multi walled carbon nanotube (MWCNT) bundles undergo blue to red electrochromism reversibly for up to 14 current cycles [9].

However, practical applications of these composites require a higher degree of control over the reversibility and critical transition voltage in these composites. Heat treatment, specifically heat treatment before polymerization has been shown to be effective to improve the ordered layer structure of PDA films [122, 123]. In this work, we investigated the effects of heat treatment on the electrochromic response of MWCNT-PDA composites. In-situ absorption and Raman spectroscopy were used to evaluate the subtle differences in the electrically induced transition of composites with and without heat treatment. Based on morphological differences, in-situ spectroscopy and Raman mapping before and after current flow, it seems like pre-heat treatment improves the chromatic response of MWCNT-PDA composites towards electrical stimulus.

To facilitate in-situ investigations, MWCNT-PDA composites were prepared through three routes as illustrated in Figure 6.1; route I yielded conventional CNT-PDA composites by the photopolymerization of DA on MWCNT sheets similar to those used

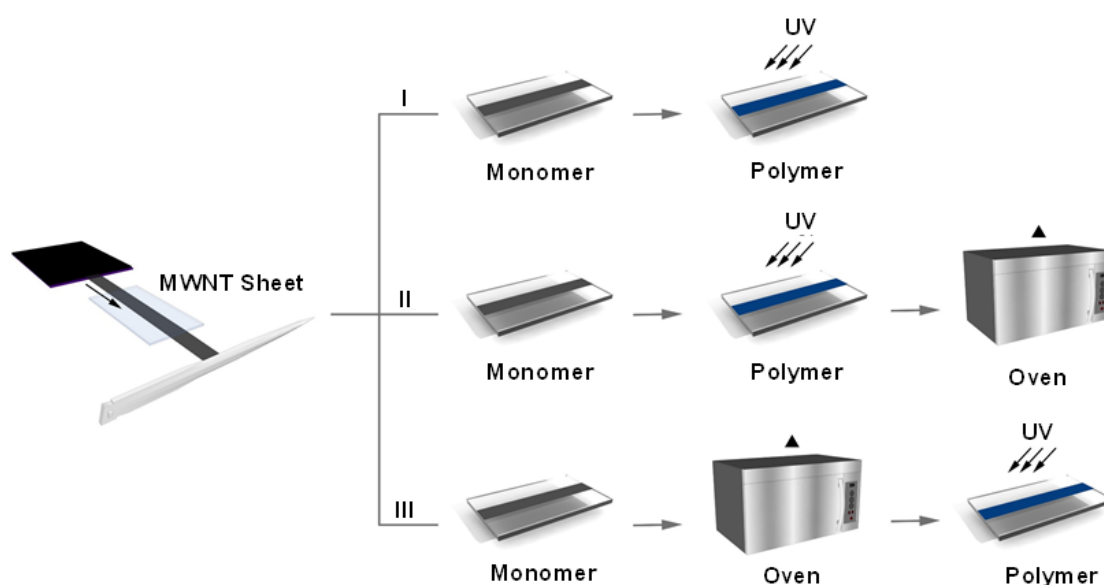


Figure 6.1 Scheme illustrating the fabrication steps for CNT-PDA composites used in this study.

in chapter 5, route II involved heating of MWCNT-PDA after polymerization and route III, heating of DA-MWCNT, prior to polymerization. Henceforth, these composites are referred to as composite I, II and III and their differences are highlighted in Table 6.1.

Table 6.1 Heat treatment processes for composites I, II and III.

Composite	Pre-heating	Post-heating
I	-	-
II	-	40° C, 1h
III	40° C, 1h	-

6.2 Morphology changes due to heating

6.2.1 Optical microscopy

The magnified images of CNT-PDA subjected to pre and post-polymerization heat treatments at different temperatures are shown in Figure 6.2. While the size of the crystalline domains appeared to decrease with increasing temperature for post-heated

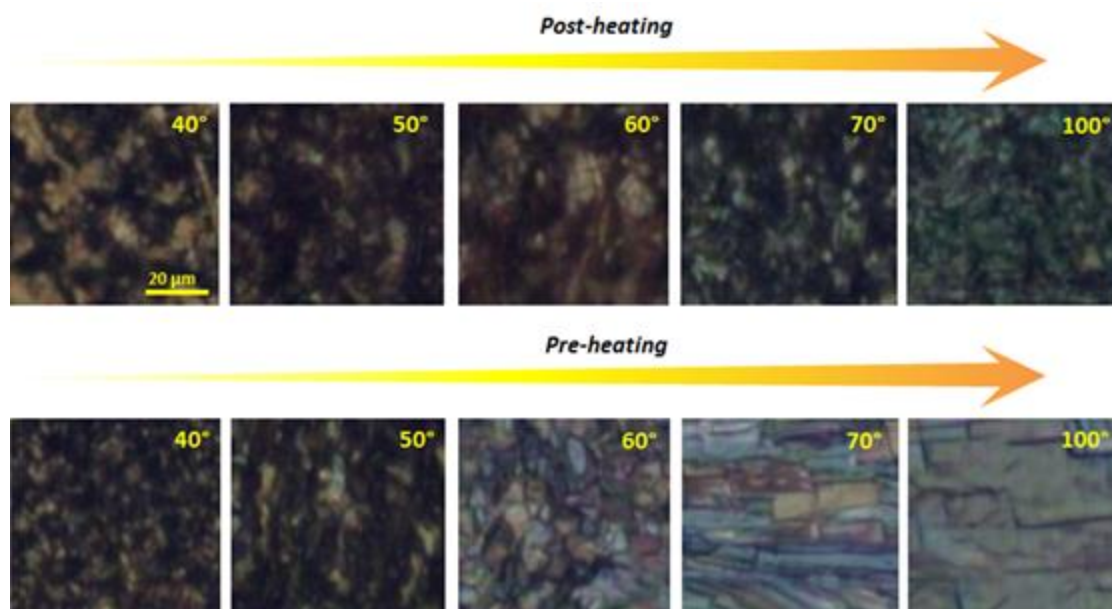


Figure 6.2 Morphology variation as observed through optical microscope as a function of post and pre-heat treatments of PDA on MWCNT sheets. The scale bar is common for all images.

composites, the domains increased in size for pre-heated composites. Although not very obvious for minor increments in temperature, this can be clearly observed in the optical micrographs corresponding to 40° C and 70° C (or 100° C) for both pre and post-heated MWCNT-PDA. Moreover, as expected, MWCNT-PDA post heated at 60° C and above appeared red due to the intrinsic blue to red thermochromism of PDA. The pre-heated composites however, always appeared blue to the naked eye, suggesting that if DA degradation occurs during pre-heating, it has very little influence on formation of blue PDA upon UV irradiation following the heating process.

6.2.2 Scanning electron microscopy

As in the case of optical microscope images, the morphology as observed through FESEM of MWCNT-PDA composites varied significantly as a consequence of heat treatment when compared to pure MWCNT sheets. Bare MWCNT sheet appeared to comprise of conducting MWCNT bundles typically of 5-10 μm in diameter. These bare MWCNT bundles also appeared bright, which is suggestive of surface charging in

conductive samples when viewed in scanning electron microscopes. Composite I appeared to have a uniform coating of polymer on MWCNT bundles (Figure 6.3b). These bundles were thicker ($\sim 20\ \mu\text{m}$) and less bright under similar imaging conditions, which is expected as PDA is not as conductive as MWCNTs. Heating of similar composites at 40°C for an hour (composite II) resulted in a structure where the polymer spread across neighboring bundles (Figure 6.3c). It is important to note that this apparent spreading is not due to PDA melting, as PDA retains its physical state at much higher temperatures ($>120^\circ\text{C}$). A similar heat treatment prior to UV polymerization (composi-

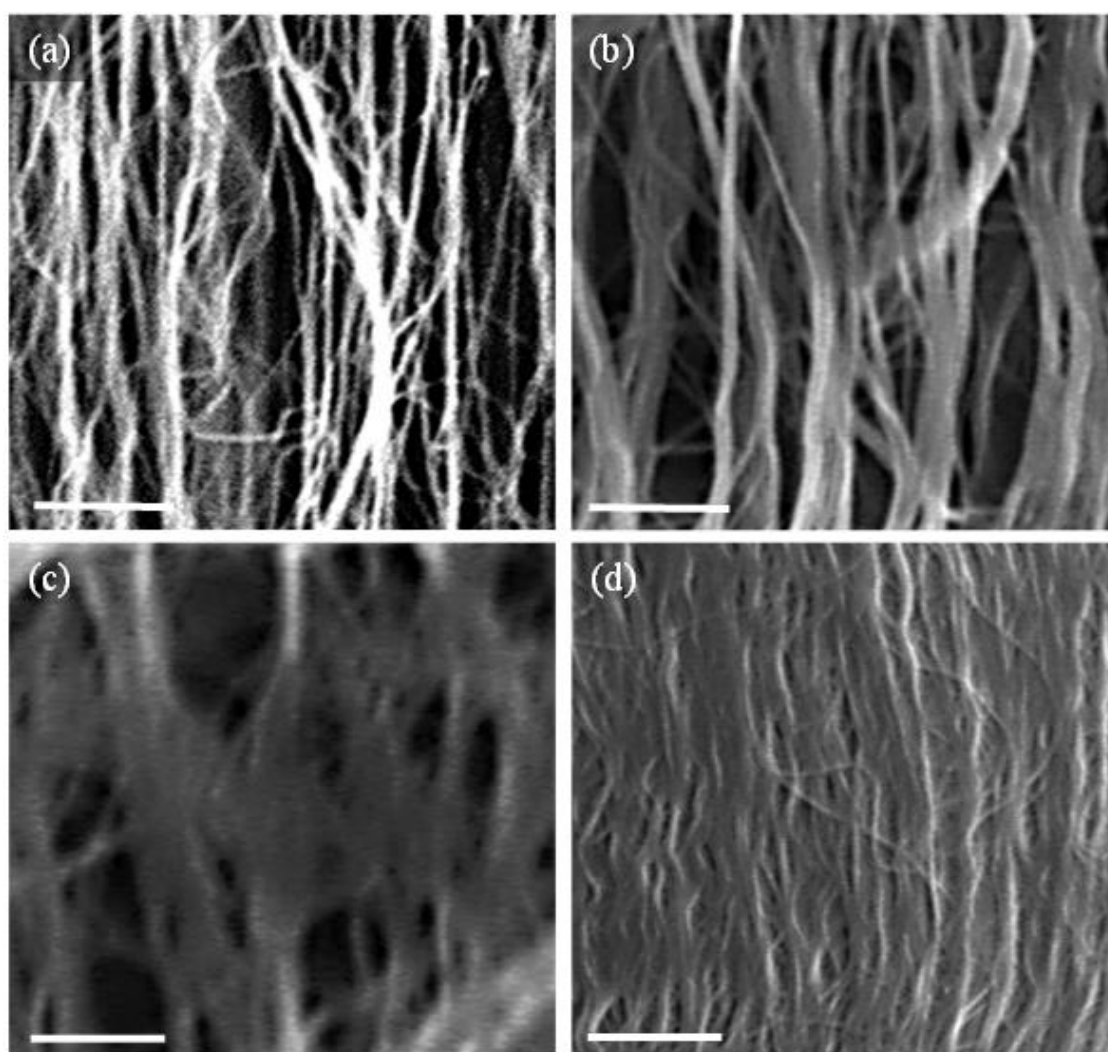


Figure 6.3 (a) Field emission scanning electron micrographs of pure MWCNT sheet, (b) PDA-MWCNT prepared through route I, (c) route II and (d) route III. The scale bar corresponds to $50\ \mu\text{m}$.

-te III) resulted in large sections of the composite with morphologies as shown in Figure 6.3d; the monomers in this case appear to have infiltrated the gaps within MWCNT bundles much more effectively prior to polymerization.

It should be noted that all subsequent in-situ spectroscopic studies were carried out on samples heated in air, at 40° C. This is because post-heating at higher temperatures (>60° C) can induce thermochromism while pre-heating at higher temperatures can induce either thermal polymerization or degradation of the monomers. Moreover, post and pre-heat treatments at 40° C revealed significant differences in PDA morphology as confirmed by both low resolution optical (Figure 6.2) and high resolution scanning electron microscopy (Figure 6.3). Thus, comparing the electrochromic response of MWCNT-PDA composites subjected to mild heat treatment (~40° C) seems sufficient to predict improvements in the electrochromic response, if any.

6.3 Heat induced order in PDA

Heat treatment has been used to improve polydiacetylene film characteristics [122, 123]. In those studies, PDA films made from DA monomers with different alkyl chain properties were heated prior to polymerization to assess the effect on thermochromism of the resulting blue PDA. They observed that the XRD peaks of PDA films obtained after pre-heating in the range of 40-60° C were way more intense than that of films resulting from un-heated DA monomers. Beyond 90° C however, the peak intensities reduced drastically and appeared similar to those of un-heated PDA films. As sharp peaks are indicative of order in the material, they associated pre-heating as a simple strategy to improve crystalline order in PDA films. Moreover, in the case of a particular PDA film prepared under strict heating conditions, the blue polymerized phase had red-shifted absorption maxima at 704 nm as opposed to typical blue PDAs

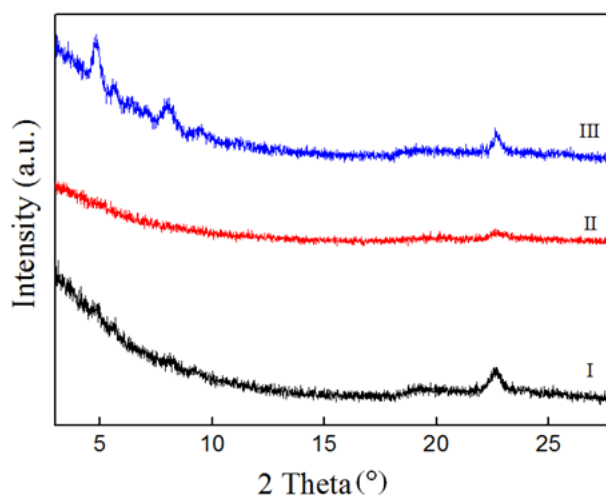


Figure 6.4 XRD patterns of composite I, II and III.

which absorb at 650 nm. This altered blue phase exhibited excellent reversibility upon removal of thermal stimulus, suggesting a link between improved order and reversible chromism in PDA.

Although post polymerization heating has not been investigated in PDAs, we expected minor structural changes to occur when PDA is heated after polymerization. These structural changes may or may not favor crystalline order in PDA, however, they could significantly influence the mode of interaction between PDA and NTs in CNT-PDA composites. The Xray diffractograms of CNT-PDA composites I, II and III were indeed different (Figure 6.4). Diffraction patterns were apparent for composites I, II and III, suggesting that PDA films generally have periodic ordered layer structures, in agreement with literature [122-124]. The intensities of the pre-heated composite (III) were much stronger, implying the ordered layer structure was enhanced upon pre-heating. Judging by the decreased intensity and broadening of diffraction peaks in the post-heated composite (II), it is obvious that the layered crystalline structure of PDA was diminished. However, as the post-heating temperature (40° C) was not high enough to induce degradation of the polymer, it is likely that the heat treatment has altered the interaction between CNT and PDA. This is confirmed from the difference in

morphologies of the composites observed through FESEM, where composite II shows spreading of PDA across CNTs while III shows a highly ordered morphology.

6.4 Linking V_c with phase transition dynamics

In-situ spectroscopy has been shown to be useful to understand the kinetics of chromatic transitions in solvatochromic and thermochromic PDA [115, 117]. In this study, MWCNT-PDA composites exposed to different heat treatments were subjected to progressively increasing voltages and their changes in absorbance recorded. Contrary to thermochromism and solvatochromism that are intrinsic to PDA, study of electrochromism in CNT-PDA requires the end to end alignment of underlying CNT sheets to be maintained. This rules out dispersing the composite in some solvent, which

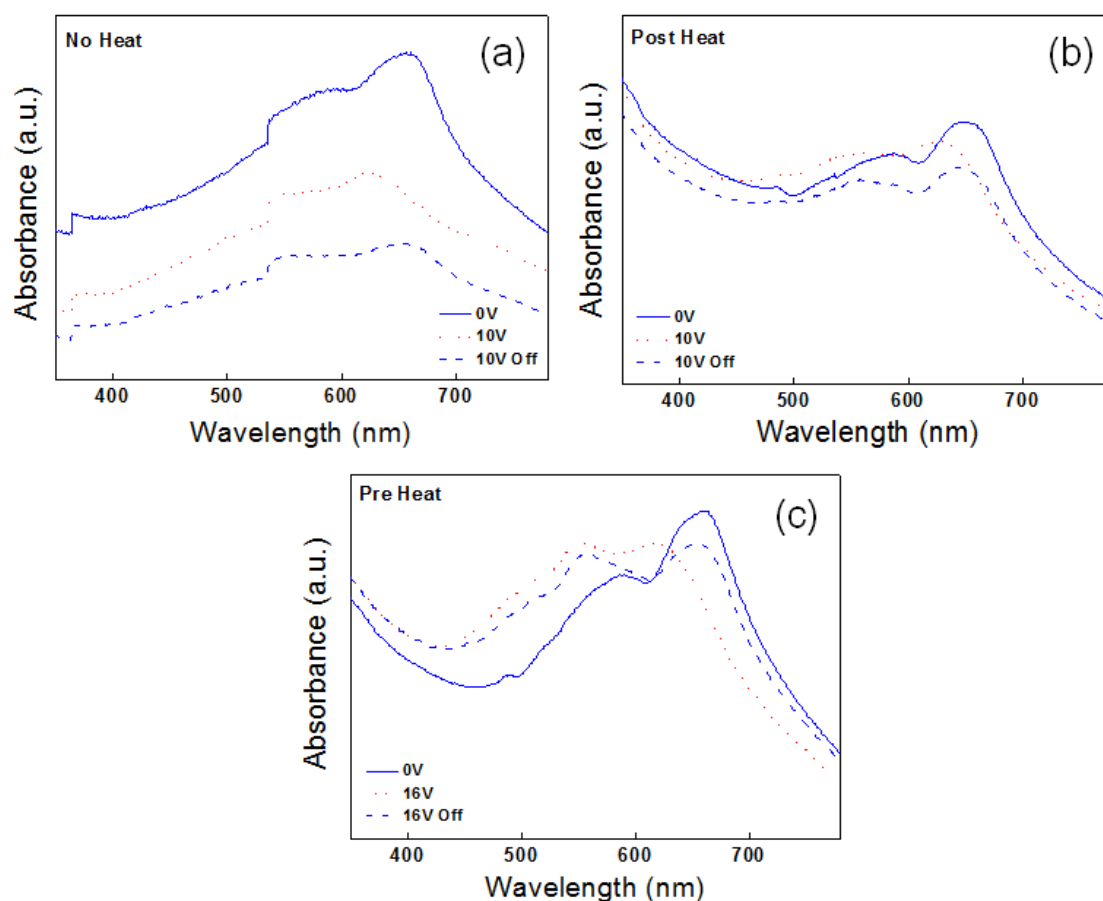


Figure 6.5 (a) In-situ absorbance change with voltage for PDA-MWCNT composite I, (b) composite II and (c) composite III.

is the typical approach for in-situ spectroscopic investigations. The modified experimental setup to investigate electrically induced blue to red transitions in CNT-PDA composites in real time is explained in detail in section 3.2.1.

Before applying voltage, all the composites, irrespective of the route of synthesis, exhibited an absorbance peak at 650 nm, which is characteristic of the blue phase of PDA (Figure 6.5). Hence, unlike the reports of Shibata et al. [122, 123], there were no red-shifted absorbance maxima for heat-treated CNT-PDA composites. Current flow caused a decrease in intensity of the blue peak and a simultaneous increase in intensity of the peak at 540 nm, characteristic of the red phase of PDA, for all cases.

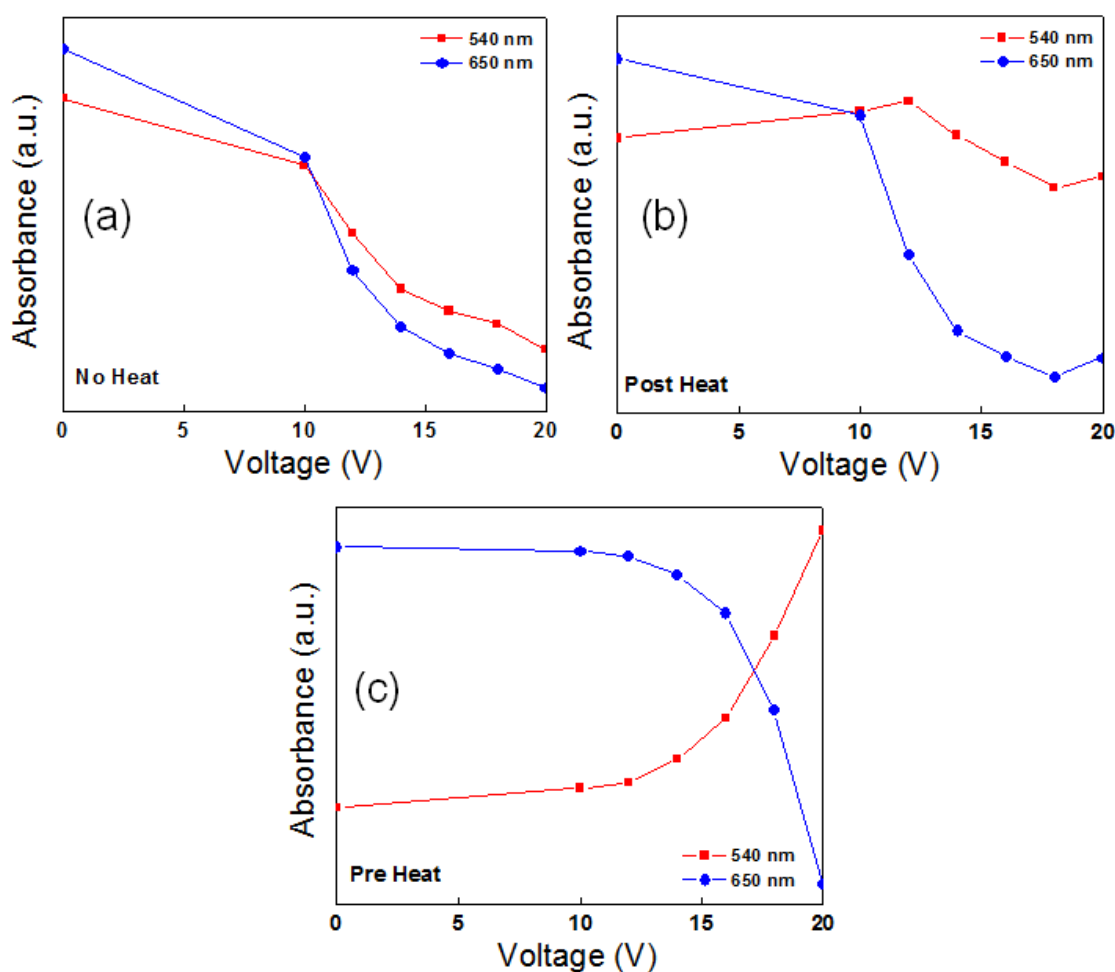


Figure 6.6 (a) Critical electrochromic transition voltages for CNT-PDA composite I, (b) composite II and (c) composite III.

However, two features of the absorbance transition stood out: (i) for composite I, current flow caused significant downward shifts of the entire absorbance spectra when compared to composites prepared through routes II and III (Figure 6.5a-c) and (ii) the critical transition voltage (V_c) increased from 10 V to 16 V for composite III, when compared to I and II (Figure 6.6a-c). V_c is estimated as the voltage at which absorbance of the red phase overshoots that of the blue phase. This information was obtained by tracking the absorbance intensities of the blue phase (650 nm) and red phase (540 nm) with increasing voltages (0 to 20 V).

Downward drift of the absorption spectra over the entire wavelength range is indicative of collective behavior of the PDA layer. This is not surprising as PDA assemblies are known to exhibit collective responses to stimuli. What is interesting is that the collective phenomenon appears to decrease substantially in the heated composites II and III. This suggests that heating, whether before or after polymerization, influences the nature of interaction between PDA and underlying MWCNTs. A possible explanation is that the PDA film breaks up into smaller, independent segments in the case of composites II while for composite III, heating facilitates orientation of DA in between MWCNT bundles prior to polymerization. Both these composites have smaller, independent PDA segments that interact more strongly with MWCNTs as opposed to composite I with larger PDA segments that have minimal interactions with MWCNTs. These observations correlate with the observed morphology differences in section 6.2.

6.5 Effect of heating on current flow

The investigations based on temperature dependence of resistivity of CNT fibers confirmed the three dimensional hopping mode of electron conduction in dry spun CNT assemblies (see section 2.10). This is very different from metallic conductors where the motion of electrons is confined in one dimension within the boundaries of the conducti-

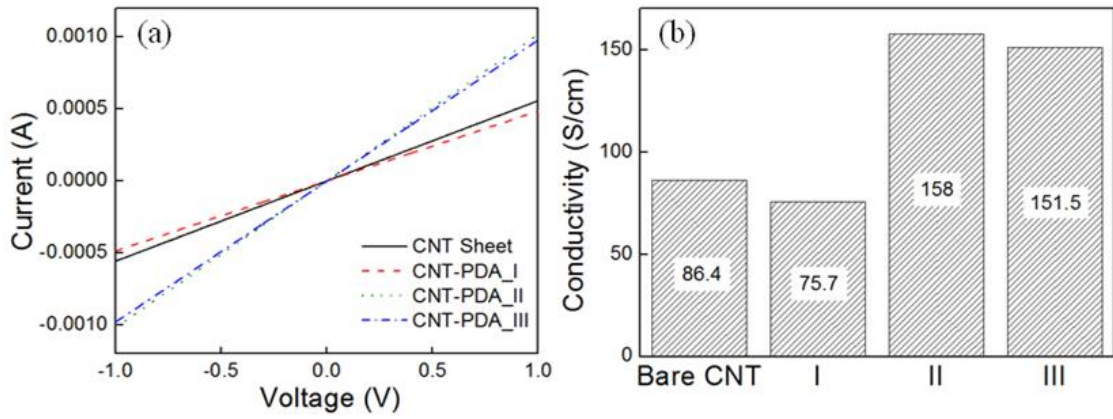


Figure 6.7 (a) Two terminal I-V plots obtained for bare CNTs, CNT-PDA, pre and post heated composites and (b) corresponding derived conductivities.

-ng element. The conjugated backbone of PDA with delocalized π -electrons give rise to similar hopping of electrons, but on a much smaller scale, as explained in section 2.12. We have now verified that heat treatment can alter the morphology and interaction between PDA and underlying MWCNTs. It is also necessary to estimate the effects of heating on the mode of current flow in these composites. After all, it is the nature and extent of three-dimensional electron hopping interactions between PDA and CNTs that result in the electrochromic blue to red transition.

The end to end alignment in CNT sheets coupled with the ease of transfer to non-conducting substrates facilitate easy current versus voltage measurements at ambient conditions. The two terminal I-V plots of bare CNT and CNT-PDA sheets with pre and post-heat treatments are shown in Figure 6.7a. All the plots appear linear, indicating good ohmic contacts between the conducting element and electrodes. Slope of the I-V plot gives conductance (G) of the material. As resistance is a function of conductor length (L), cross sectional area (A) and resistivity (ρ), it was possible to derive the conductivity (σ) as:

$$\sigma = \frac{1}{\rho} = \frac{L}{R \cdot A} \quad (6.1)$$

From Figure 6.7b, it appears that incorporating less conductive PDA on conducting CNT sheets reduces conductivity (from 86.43 to 75.75 S/cm). Heat treatment (pre and post polymerization) significantly improved conductivity, suggesting that three dimensional electron hopping becomes more efficient. However, the morphological differences between pre and post-heated composites suggest that the enhancement in conductivity does not result from the same processes. In composite II, as PDA spreads across MWCNT bundles, more of the polymer, comes into contact with MWCNTs. This means that there is more chance of interaction between delocalized electrons of the conjugated PDA and MWCNT networks. In composite III however, the increased interaction of delocalized electrons results not from PDA spreading but rather, from the polymerization of DA in the fine gaps between MWCNT bundles as well as on the surface.

6.6 PDA realignment comparison

The conjugated nature of the back-bone of PDA makes it ideal for characterization using Raman spectroscopy as double and triple bonds of carbon give distinct Raman shifts at around 1450 and 2080 cm^{-1} , respectively [116]. Typically, red phase of PDA exhibits red-shifted peaks for both $\nu_{\text{C}=\text{C}}$ and $\nu_{\text{C}\equiv\text{C}}$ [118]. Moreover, changes in the intensity of the Raman signal are suggestive of PDA alignment changes; intense peaks imply PDA is aligned along the laser polarization direction while weak peaks indicate the opposite. Due to the aligned nature of underlying MWCNT sheets used in this work, the laser polarization direction coincides with the axis of MWCNT sheets. Hence, in-situ tracking of the intensity and shift of the prominent carbon peaks from PDA could reveal a lot about the physical aspects of the chromatic transition in MWCNT-PDA composites.

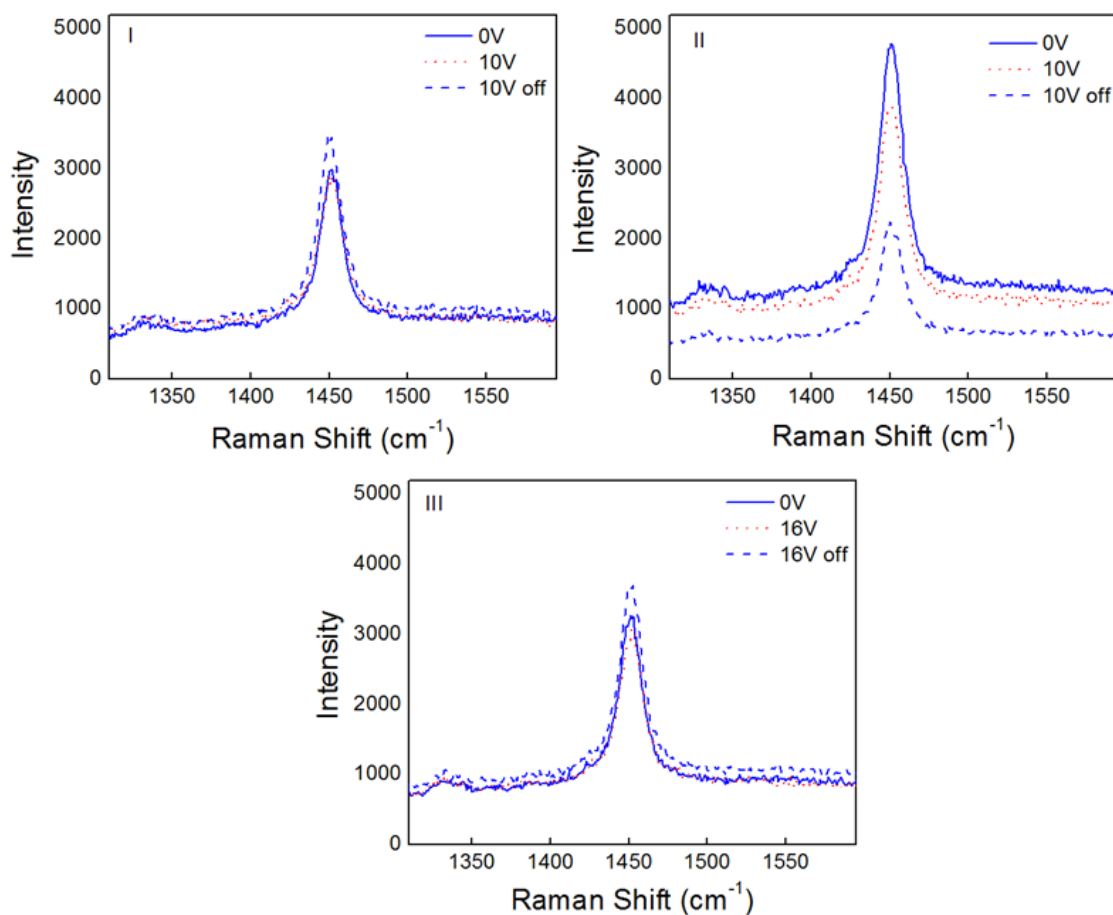


Figure 6.8 Evolution of $\nu_{C=C}$ of MWCNT-PDA composites prepared via route I, II and III, before, during and after the critical transition voltage.

It should be noted that in this in-situ Raman investigation, point spectra centered at 1450 cm^{-1} was obtained, as $\nu_{C=C}$ is the most prominent peak in the PDA Raman spectrum. We learnt from the in-situ absorption studies that the critical transition voltage for composites I and II was 10 V while that for III was 16 V. The $\nu_{C=C}$ of these composites before, during and after removing 10 V (for I and II) and 16 V (for III) were thus compared. The Typical peak profiles before, during and after applying the critical transition voltage for composite I, II and III are shown in Figure 6.8. The most striking observation was that before applying voltage bias, the intensity was highest for composite II (Table 6.2). This corresponds to the morphology observed through FESEM, where the PDA segments appear to spread across neighboring bundles.

Table 6.2 Comparison of the Raman shifts and intensities before during and after application of critical transition voltage in composites made through routes I, II and III.

Composite	Voltage (V)	$\nu_{C=C}$ (cm^{-1})	Intensity (Counts)
I	0	1451.93	2161.65
	10	1450.11	2069.45
	10 Off	1449.21	2547.66
II	0	1452.68	3772.82
	10	1450.87	2775.27
	10 Off	1449.96	1620.62
III	0	1451.02	2333.68
	16	1451.93	2129.58
	16 Off	1452.84	2659.17

A closer look at the peaks under voltage bias reveals that for composites I and III, there was hardly any difference in intensity while for II, the intensity decreased substantially (3772.82 to 2775.27). Removal of voltage bias caused an increase in peak intensities for I (2069.45 to 2547.66) and III (2129.58 to 2659.17), while for II, caused a drastic decrease (2775.27 to 1620.62). Details of the Raman shift and intensity variations under current flow are listed in Table 6.1. As mentioned earlier, peak intensity is indicative of the alignment of PDA on MWCNT, with high intensities suggesting more PDA is aligned along the laser polarization (MWCNT) direction. Hence, from the peak profiles in Figure 6.8, it can be interpreted that post-heat treatment improves the degree of

motion of PDA chains under electrical stimulus, but hinders recovery of initial PDA alignment upon removal of stimulus. Pre-heat treatment however does not improve the degree of motion of PDA chains, but slightly improves the ability of PDA to change alignment along MWCNT upon stimulus removal. In terms of recovering the initial alignment of PDA upon removal of electrical stimulus, heat treatment seems to have no positive effect.

6.7 Quantifying interaction between CNT and PDA

The strong Raman shifts originating from the conjugated backbone of PDA permits mapping of a specified area of the composite sample to gauge the polymer distribution pattern, which is difficult using conventional microscopic techniques. As

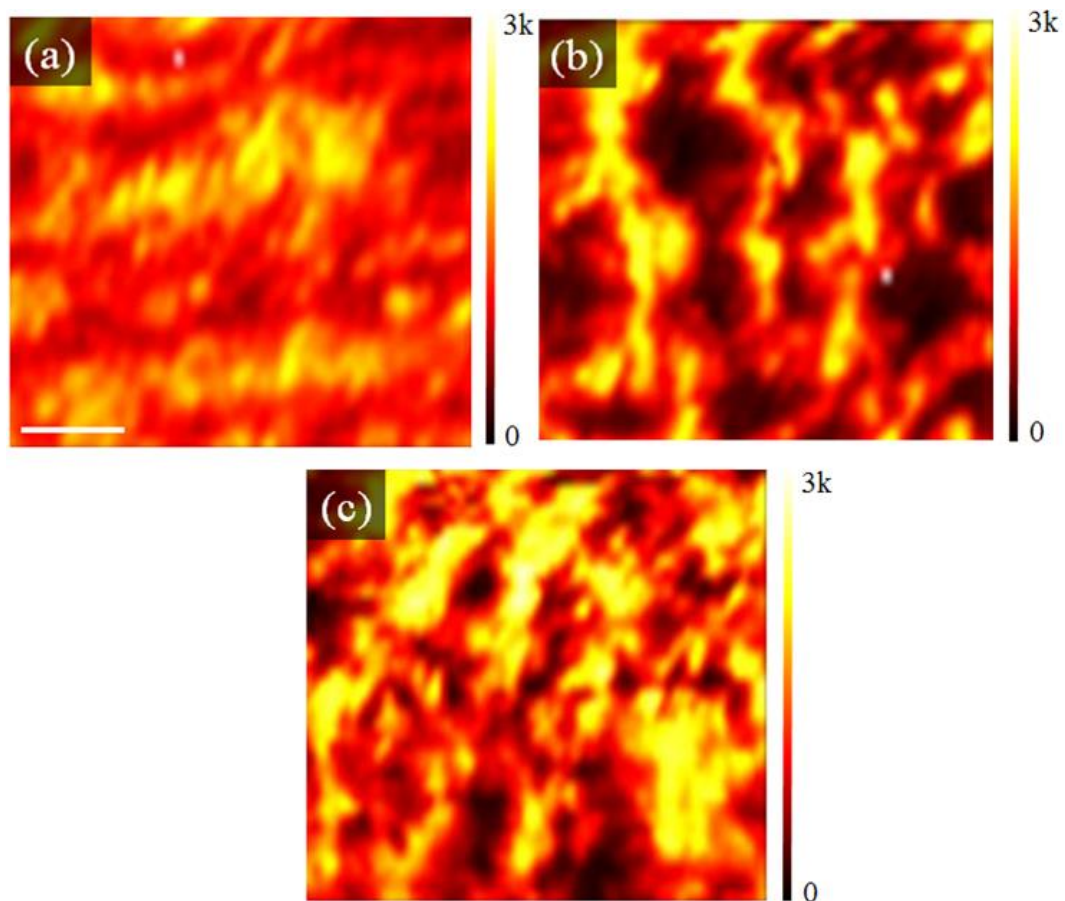


Figure 6.9 (a) Raman map images for composites via route I, (b) route II and (c) route III. The horizontal scale bar corresponds to 20 μm and is common for all maps. The vertical scale bars correspond to the $v_{\text{C}=\text{C}}$ intensity.

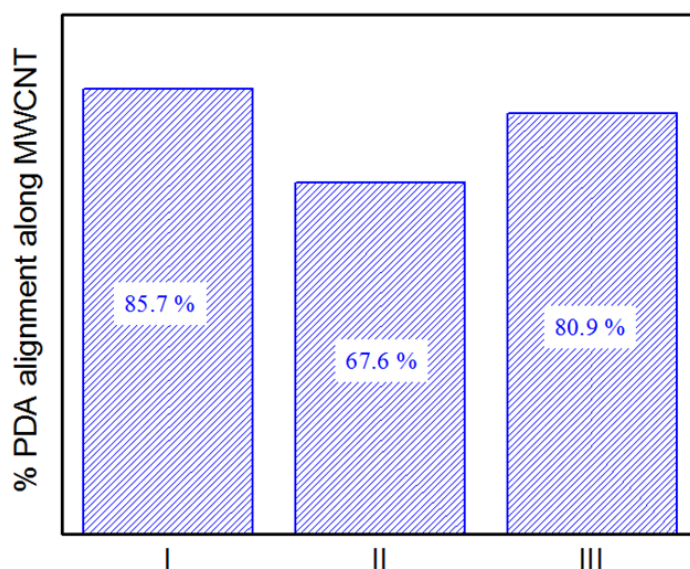


Figure 6.10 Calculated percentage alignment of PDA along underlying MWCNTs in composites I, II and III.

the incident laser beam (633 nm) is polarized along the horizontal axis (along the MWCNT alignment direction for our composites), intense Raman peaks imply the PDA is aligned along the laser polarization direction, i.e. along the MWCNTs. We tracked the intensity of the most prominent PDA peak, $\nu_{C=C}$ at 1450 cm^{-1} , over an area of $50\text{ }\mu\text{m}^2$.

The Raman maps obtained for composites I, II and III in the blue phase are shown in Figure 6.9. All maps had distinct bright regions, which denote the regions where polymer segments aligned along the laser polarization direction, as explained earlier. Further visual inspection on the maps reveal that in the absence of heating (composite I), though large sections of PDA are not aligned perfectly along the polarization direction, almost all of the underlying MWCNT surface is covered by PDA. Upon heating (composites II and III), the PDA layer seems to break up and aggregate in certain sections on the MWCNTs, leaving other regions completely devoid of PDA coating, as evidenced by distinct black regions in the maps.

By quantifying the bright sections of these maps using the threshold feature of ImageJ software, we found that composites I, II and III had 85.7, 67.6 and 80.9 % of PDA aligned the underlying MWCNTs (Figure 6.10). This observation seems reasonable taking into consideration the morphological differences induced by heating described in section 6.2. It has to be noted that the black sections in the map of composite III are not due to PDA breaking up as a result of heating, as heating is carried out prior to polymerization. Instead, these black sections are more likely due to the lack of favorably aligned DA monomers after pre-heating. Monomers in those regions either fail to polymerize upon UV irradiation, and result in weak Raman signals, if any.

The absorption spectra of composite I underwent drastic downward drift over the entire wavelength range and removal of the critical transition voltage further enhanced the downward drift (Figure 6.5a). This suggests that the PDA layer of I shows a collective behavior, with the absorption of the entire film reducing irreversibly under current flow. While the downward drift occurs for composites II and III, the magnitude of the drift is considerably reduced (Figure 6-5b and c). In fact, the drift is almost negligible in the blue end of the spectra for composite III. It thus seems likely that heat treatment (both before and after UV irradiation) reduces the ability of the PDA layer to respond collectively. This could be a consequence of the altered PDA and MWCNT interaction in composites II and III as evidenced by the FESEM images.

6.8 Mechanistic interpretation

Although heat treatment reduces the collective response of MWCNT-PDA composites, the significant increase in critical transition voltage of composite III points towards a different transition dynamic in this case. De-stacking of π -orbitals at the MWCNT-PDA interface is the likely origin of electrochromism in these composites [125]. If the transition proceeds at a lower voltage, it means that de-stacking of π -orbitals

occurs fairly easily. In our case, composites I and II undergo the transition at 10 V while III, at 16 V (Figure 6.6a-c). Hence, de-stacking of π -orbitals requires a higher current flow for composite III. This is unexpected as pre-heat treatment seems to improve the interaction between PDA and MWCNT (Figure 6.3d), implying a more efficient interaction of π -electrons at the interface, and consequently, de-stacking at lower potential bias. A likely explanation is that the PDA segments in composite III are much smaller than the other two cases. Electrochromic transition in such a system will require de-stacking of π -orbitals of a large number of small PDA segments as opposed to few

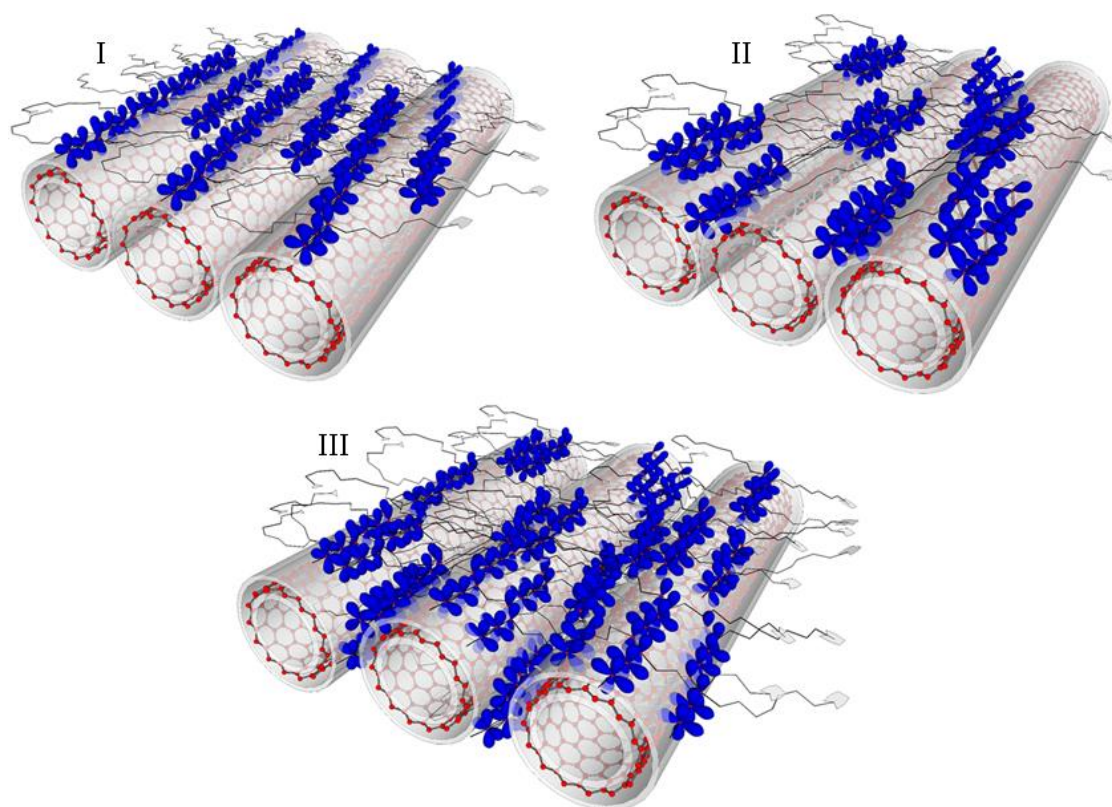


Figure 6.11 (I) Proposed structures of MWCNT-PDA composites with no heat treatment, (II) post-heat treatment and (III) pre-heat treatment. UV irradiation produces a surface coating of PDA on underlying MWCNTs (I). Post-heat treatment breaks up large PDA segments and spreads them across neighboring MWCNT bundles (II). Pre-heat treatment facilitates intercalation of monomers into the gaps between MWCNT bundles, resulting in high π -stacking interactions at the MWCNT-PDA interface after UV irradiation (III).

large segments in composites I and II, accounting for the increased critical transition voltage.

Based on the morphological analysis and spectroscopic results, we propose the following structural differences in MWCNT-PDA composites I, II and III. For composite I, UV irradiation results in long PDA segments aligned more or less along the axis of underlying MWCNT. Heat treatment after polymerization breaks up the large segments and spreads them across neighboring MWCNT bundles in the case of composite II. When heat treatment precedes the UV polymerization process (Composite III) the DA monomers aggregate as small clusters which align along MWCNTs as well as intercalate the gaps between bundles, with a high degree of stacking.

The effectiveness of non-covalent interaction between the polymer and MWCNT, or in other words, π -stacking efficiency, is likely to be significantly influenced by these structural changes induced by heat treatment treatments. We expect the π -stacking to be minimum in composite I, where the DA monomers simply aggregate along the MWCNT sheet prior to UV irradiation. Heat treatment after polymerization as in the case of composite II, spreads the broken up polymerized segments across neighboring MWCNT bundles, with an accompanied slight increase in π -stacking at the interface. When heat treatment precedes UV polymerization (composite III), the DA monomers intercalate between neighboring MWCNT bundles, resulting in a structure with much higher π -stacking efficiency than I and II, after UV polymerization. However, the considerably reduced collective behavior of the PDA layer in III suggests that the PDA segments are much shorter than I and II. A higher critical transition voltage is required in this case to cause de-stacking in many small PDA segments as opposed to few large PDA segments in I and II, to realize the electrochromic transition. The proposed structural differences are illustrated in Figure 6.11.

6.9 Summary

The effects of heat treatment on the electrochromic response of MWCNT-PDA composites were investigated. Morphology comparisons revealed the possible breaking up and spreading of large PDA segments onto neighboring MWCNT bundles after heat treatment. In-situ absorption studies revealed a direct link between critical transition voltage and heat treatment, with pre-heated MWCNT-PDA composites exhibiting a higher critical transition voltage of 16 V as opposed to 10 V for both un-annealed and post-annealed composites. Evolution of Raman shift $\nu_{C=C}$ before, during and upon removal of the critical transition voltage suggested that post heat treatment improved the degree of motion of PDA chains. We propose that pre-heat treatment increases V_C of MWCNT-PDA composites owing to a structure with high degree of π -stacking, brought about by monomers intercalating the gaps between MWCNT bundles prior to photo polymerization.

Chapter 7 Reversible electrochromism in CNT-ZnO-PDA composites

7.1 Introduction

A systematic review of literature dealing with chromism in PDA has revealed that the blue to red transition can be reversible when (i) strong aromatic interactions, (ii) ionic interactions, (iii) covalent interactions and (iv) multiple hydrogen bonds are present in the PDA microstructure [48]. The typical route to incorporate these changes in PDA is through chemically altering the PDA, which is complicated and expensive. However, it has been demonstrated that ZnO nano particles can act as anchoring sites for PDA through ionic interactions, and influence the chromatic transition process, through a straight forward, cheap synthesis process. Research efforts along this direction have yielded PDA-ZnO hybrids capable of partly reversible and fully reversible thermochromic transitions [126-130]. Despite the positive results regarding chromatic reversibility of PDA-ZnO structures, there is no report of electrochromism of CNT-ZnO-PDA hybrids in literature. This chapter summarizes our efforts to investigate the role of ZnO nano particles on the electrochromic transition dynamics of CNT-ZnO-PDA hybrids.

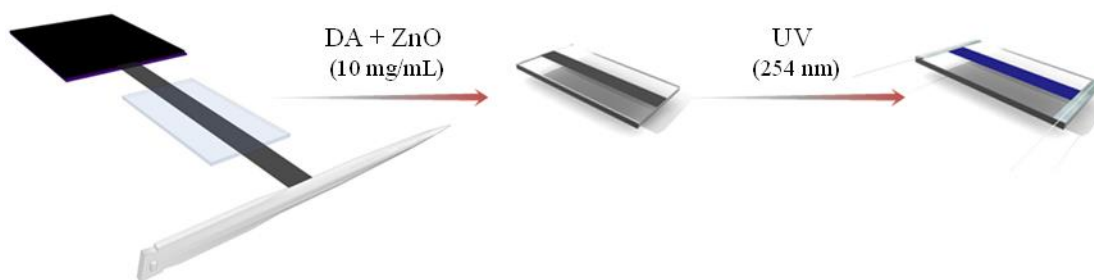


Figure 7.1 Steps involved in the fabrication of CNT-ZnO-PDA hybrids.

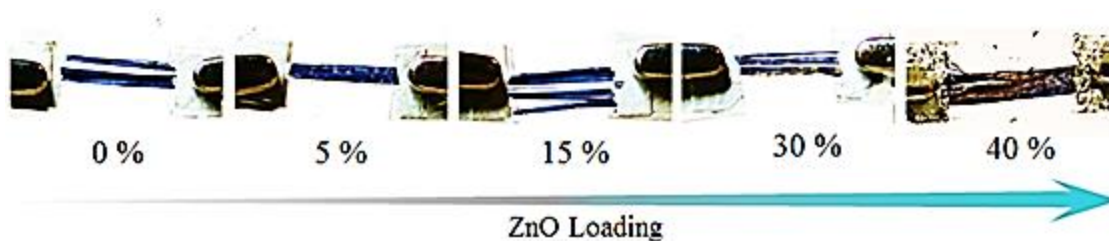


Figure 7.2 Photographs of CNT-ZnO-PDA hybrids with increasing loading of ZnO.

Samples were prepared in a similar manner as described in Chapter 4, with the sole difference being the incorporation of ZnO nanoparticles into the monomer solution. The steps involved are illustrated in Figure 7.1. ZnO loading was increased as high as 40 % by volume to gauge whether ZnO influences the polymerization to yield blue colored state of the hybrid prior to electrical stimulus. However, as evident from Figure 7.2, it was clear that even hybrids heavily loaded with ZnO appeared blue to the naked eye, similar to PDA-CNT composites prepared earlier. We noticed that even though highly loaded CNT-ZnO-PDA exhibited the expected blue to red absorbance changes, the contrast of the colored states reduced with ZnO concentration. Moreover, 5% by volume loading of ZnO was considered more than sufficient to influence the chromatic properties of PDA in the previous reports [126-130]. Hence, all experiments in the following sections were carried out on the hybrid with 5 % ZnO loading.

7.2 Morphology and Characterization

As in the case of CNT-PDA composites used in chapters 5 and 6, the surface morphology of the CNT-ZnO-PDA hybrids were investigated using FESEM (Figure 7.3). The hybrid appeared to have uniform coating over the MWCNT bundles. At first glance, there appears to be not much difference between the morphologies of CNT-ZnO-PDA (Figure 7.3b) and CNT-PDA composites (Figure 6.3b), which suggests that introducing ZnO np's does not hinder the polymerization of DA on MWCNT surface..

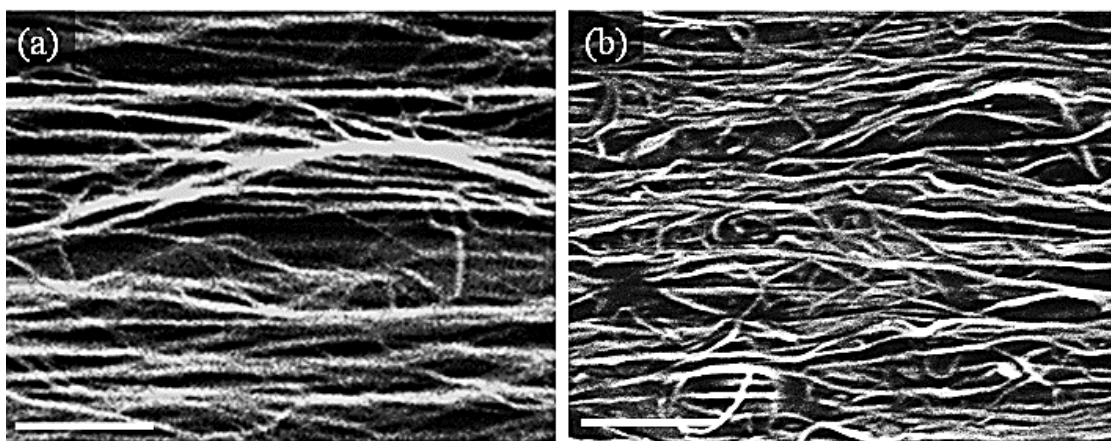


Figure 7.3 FESEM micrographs of (a) MWCNT bundles and (b) CNT-ZnO-PDA hybrids with 5 % ZnO loading. The scale bar corresponds to 50 μm .

It does however seem like the polymerized bundles are comparatively thinner in the CNT-ZnO-PDA hybrids, comparable to the CNT-PDA structure obtained after pre-heating (Figure 6.3d). This may be considered as evidence that ZnO facilitates a more uniform distribution of DA monomers between and upon MWCNT bundles aligned in the horizontal direction prior to photopolymerization, even without any pre or post-heat treatments. The extent of ZnO loading could not be verified with FESEM. This is probably due to the fact that PDA polymerizes over the ZnO and MWCNTs, hiding the ZnO nanoparticles incorporated in the monomer solution. However, XPS studies carried out on the hybrids confirm the presence of ZnO (see section 7.7)

XRD and TEM analysis of the ZnO powder used in this study confirms the crystalline structure with an average particle size of 100 nm (Figure 7.4). The diffraction peaks in Figure 7.4a could be easily indexed to the hexagonal phases of ZnO. As the diffraction peaks were sharp and intense, the ZnO np's are expected to be extremely crystalline. It should be noted that there was significant agglomeration of the ZnO np's and thus, particle size and shapes could vary over a broad range in the prepared hybrids.

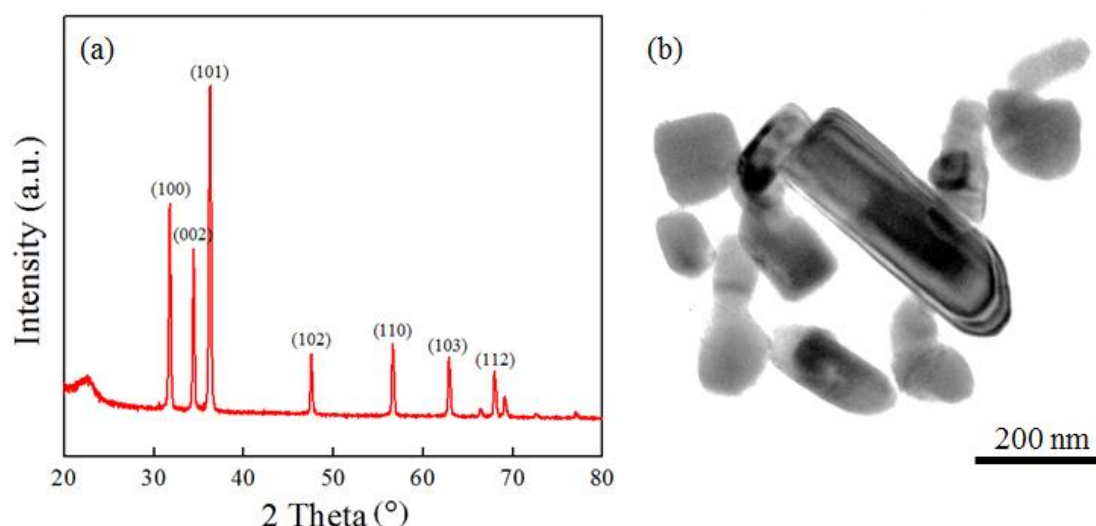


Figure 7.4 (a) Xray Diffractogram of ZnO nanoparticles incorporated in the hybrids used in this work and (b) typical transmission electron microscope image of ZnO np's, confirming the average particle size ~100 nm.

7.3 Reversibility of phase change in CNT-ZnO-PDA

The in-situ spectral transition was recorded with voltage increments from 0 V to 20 V to estimate the critical transition voltage in CNT-ZnO-PDA hybrids. Absorbance values of the two dominant peaks, 650 nm for the blue phase and 540 nm for the red phase, were tracked. From the tracked data illustrated in Figure 7.5a, we learnt that the blue to red transition in CNT-ZnO-PDA hybrids was triggered around 7 V, which is lower than that expected for conventional CNT-PDA composites prepared via similar route (see section 6.4). Even heat-treatments carried out to improve PDA structure did not result in V_c as low as 7 V. It stands to reason that incorporating ZnO improves three dimensional electron hopping interactions between the conjugated PDA and MWCNTs, resulting in the electrochromic transition occurring at a lower voltage than expected. More importantly, the transition appeared to be partly reversible for the hybrids (Figure 7.5b) as opposed to conventional CNT-PDA composites (Figure 6.5a). Hence, the in-situ variation in absorbance indicate that CNT-ZnO-PDA hybrids are more likely to

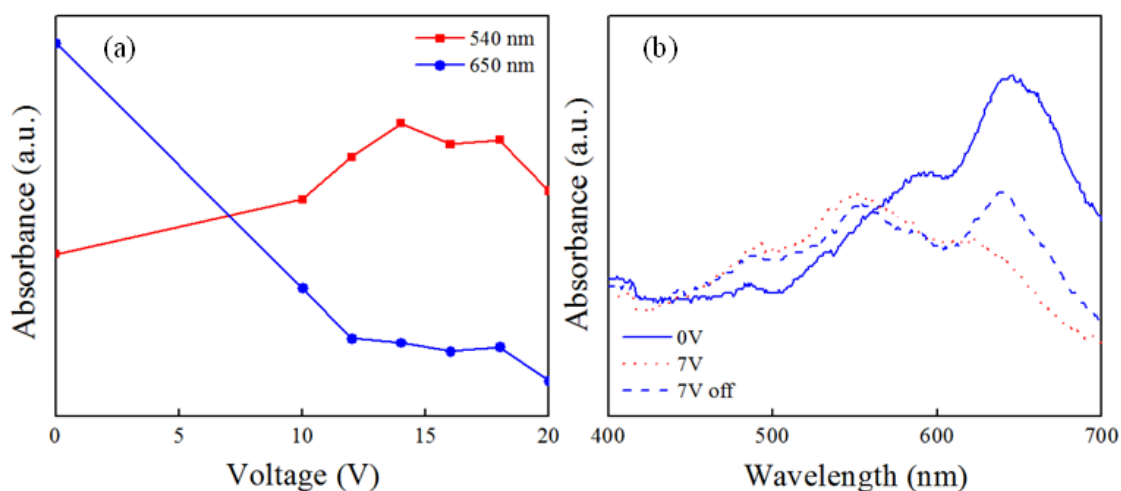


Figure 7.5 (a) Tracking of main peak absorbances for the blue and red phase of CNT-ZnO-PDA hybrid and (b) estimating the reversibility of the transition in the hybrid at critical transition voltage of 7 V.

reversibly respond to electrical stimulus, with significant recovery of the blue phase upon removal of current.

7.4 PDA alignment before and after current flow

The strong Raman shifts originating from the conjugated backbone of PDA are an indirect indicator of the alignment of PDA with respect to the underlying MWCNTs. This is due to the fact that the horizontally aligned MWCNT sheets are made to orient along the incident laser polarization direction. Hence, under the same laser irradiation conditions (laser power and focus region) and sample orientation, a sharp and intense peak implies that the PDA back bone is aligned along the MWCNT direction while a less intense peak is suggestive of some degree of alignment change.

As electrical contacts were provided with conductive silver paint prior to Raman studies, it was possible to visualize peak intensity variations before, during and after current flow by using a standard DC power source with customized probes. As in the previous study, the most prominent PDA peak ($\nu_{C=C} \sim 1450 \text{ cm}^{-1}$) was investigated. From the in-situ Raman shifts at the critical transition voltage for the hybrid (7 V), it was

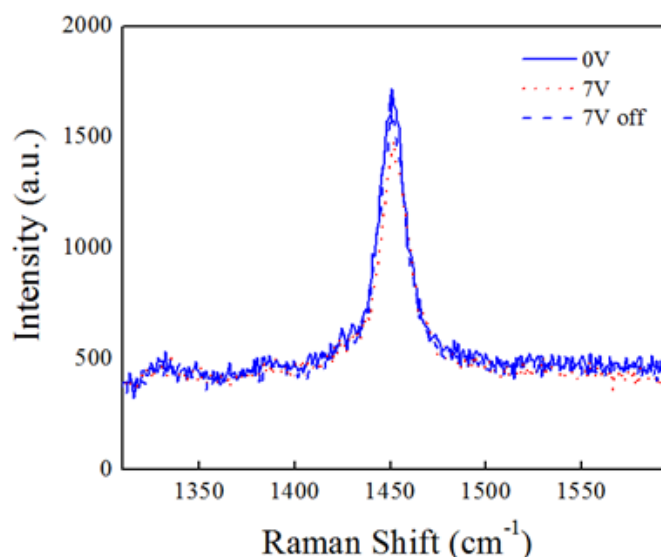


Figure 7.6 In-situ Raman point spectra for the hybrid based on $v_{C=C}$ obtained before, during and after application of critical transition voltage of 7 V.

evident that current flow resulted in a reduced peak intensity (1247.49 to 1030.21), which recovered almost completely (1030.21 to 1231.96) upon switching off current (Figure 7.6).

This behavior is similar to that of conventional CNT-PDA composites with and without pre-heat treatment (Figure 6.8a and c). However, it should be noted that for those composites, switching off current resulted in a peak intensity higher than that before current flow, which means that there was considerable difference in the PDA alignment before and after current flow, unlike the hybrids where the intensities appear to be almost identical before and after current. Moreover, the Raman shifts in the hybrid tend to revert to the initial position (1450.87 cm^{-1}) after current flow (1451.78 to 1449.96 cm^{-1}) (Table 7.1). This is in contrast to conventional CNT-PDA composites where the Raman shifts undergo either blue shifts or red shifts, but never tend to revert to the initial position when the current flow stops (see Table 6.1 in section 6.6). Hence, it appears that incorporation of ZnO does indeed assist in restoring the original alignment of PDA upon removal of the electrical stimulus.

Table 7.1 Comparison of Raman shift and intensity variations before, during and after applying critical transition voltage in CNT-ZnO-PDA composites.

Voltage (V)	$\nu_{C=C}$ (cm^{-1})	Intensity (Counts)
0	1450.81	1247.49
7	1451.78	1030.21
7 Off	1449.96	1231.96

7.5 Confirming blue phase recovery in CNT-ZnO-PDA

Apart from point Raman spectra, it is also possible to scan a specific area of the sample for a particular peak to generate a map profile. Raman mapping is advantageous in our cases as we can distinctly observe the features relevant to PDA alone by choosing the appropriate incident laser power. This is so because MWCNTs and ZnO, the other components that form our samples, require a much higher laser power ($\sim 10\%$) compared to PDA (0.05%) to exhibit strong Raman signals. Moreover, as the measurement is carried out in ambient conditions, we can provide electrical connections to a DC source to obtain accurate maps of specific regions, before and after current flow. Such measurements are much more complicated to be carried out using high resolution microscopy techniques such as SEM, which require high vacuum conditions. As usual, we chose the most prominent feature of the PDA Raman spectrum ($\nu_{C=C}$ at $\sim 1450\text{ cm}^{-1}$) for the mapping process.

The Raman maps obtained before and after applying the critical transition voltage for conventional CNT-PDA composites and the CNT-ZnO-PDA hybrids are shown in Figure 7.7. Bright yellow/white regions (seen in Figure 7.7a, c and d) represent PDAs aligned along the laser polarization (MWCNT) direction. It was obvious that

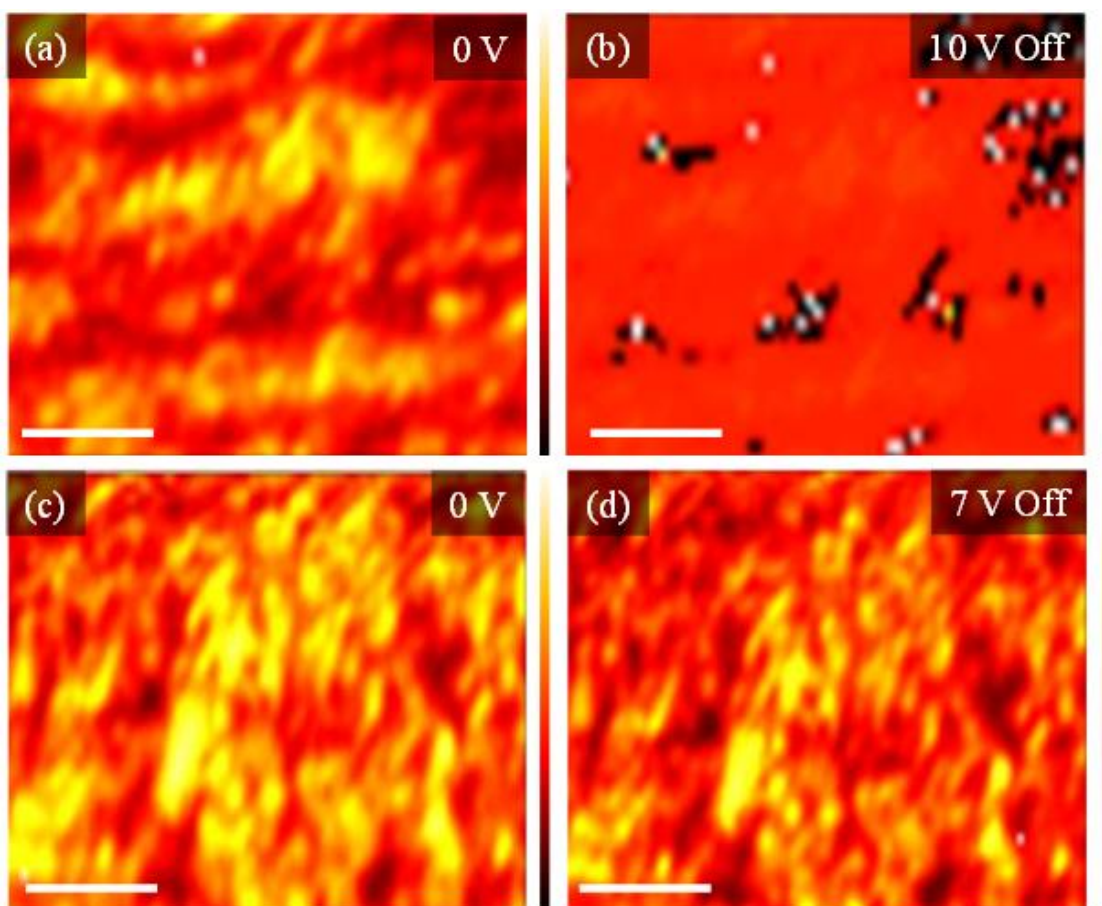


Figure 7.7 (a) Raman map before and (b) after current flow in CNT-PDA and (c) the corresponding Raman map before and (d) after current flow in CNT-ZnO-PDA hybrid. The horizontal scale bar corresponds to 20 μm . The vertical scale bar corresponds to Raman intensity (0 as black and 3k as white).

CNT-PDA composites underwent wide spread, collective changes in the maps after current flow (Figure 7.7b). ImageJ Analysis of the maps obtained prior to current flow suggested approximately 86 % and 92% alignment of PDA in the conventional composite and the CNT-ZnO-PDA hybrid, respectively.

For the hybrid however, the maps appeared largely similar before and after current flow (Figure 7.7c and d), with bright regions persisting even after current flow. Hence, whatever alignment change in PDA was induced during current flow, was restored when the current flow stopped. The only possibility for recovery of PDA alignment seems to be the anchoring effect brought about by ZnO np's. As it has been

verified previously that PDA realignment induced π -destacking is the likely origin of electrochromism, this result confirms that there is indeed improved reversibility of current induced PDA realignment in the CNT-ZnO-PDA hybrids.

7.6 Improved conductivity in CNT-ZnO-PDA

In a manner similar to that explained in section 6.5, the conductivity of CNT-ZnO-PDA composites was compared with bare CNTs (Figure 7.8). The slope of the two terminal I-V plots obtained from a single long sheet of MWCNTs, cut into different parts and incorporated with PDA and ZnO-PDA solutions revealed interesting trends. On incorporating less conductive PDA onto MWCNT sheet, the slope of the I-V plot decreased from 5.57×10^{-4} to 4.85×10^{-4} , while incorporating ZnO-PDA onto MWCNTs, the slope increased to 1.21×10^{-3} .

Using the conductance values obtained from the I-V plots, it was possible to calculate and compare the conductivity of the composites. The conductivity enhanced significantly (from 86.4 to 188.7 S/cm) in CNT-ZnO-PDA hybrids. This enhancement is even more than that of heated CNT-PDA composites (see section 6.5). Hence, not only does ZnO improve the recovery of initial alignment of PDA through surface anchoring, it also improves three dimensional electron hopping from MWCNTs to PDA.

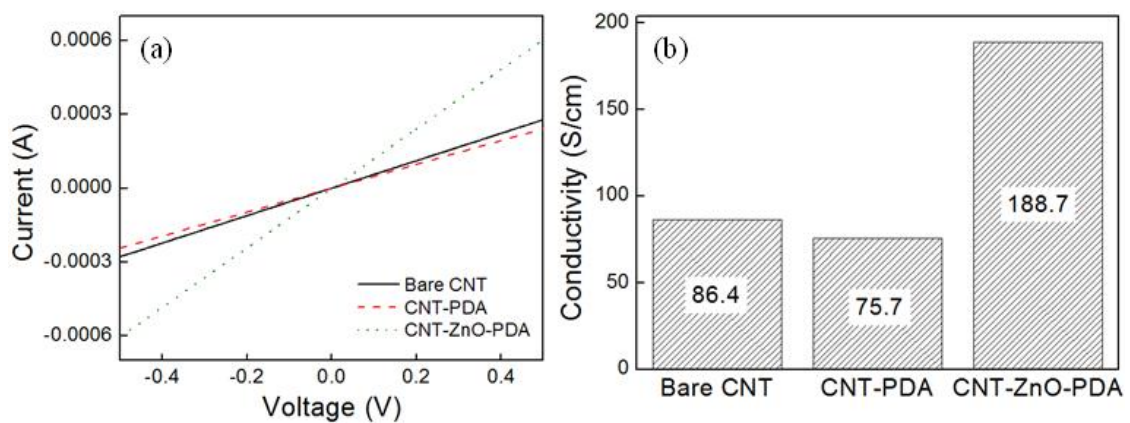


Figure 7.8 (a) Two terminal I-V plots obtained for bare CNT sheet, CNT-PDA and CNT-ZnO-PDA and (b) the corresponding derived conductivity values.

This improved electron interaction is one possible reason for the comparatively lower critical transition voltage in these hybrids, as opposed to conventional CNT-PDA and heat treated CNT-PDA composites.

7.7 Mechanistic interpretation of phase change in CNT-ZnO-PDA

XPS is extremely useful to understand the dependence of material properties at external and internal interfaces. This is significant for hybrids such as CNT-ZnO-PDA used in this work as PDA is expected to interact with the ZnO surface through ionic interactions (OH^- and O^+) as well as with the conjugated MWCNT surface through π -stacking.

XPS survey scans of the CNT-ZnO-PDA hybrid, before and after current flow, are shown in Figure 7.9, with the Zn 2p peaks highlighted. The acquired spectra were calibrated with respect to the C 1s peak at 285 eV. The Zn $2p_{3/2}$ peak (see insets in Figure 7.9a and b) occurring at a binding energy position ~ 1021 eV is attributed to Zn-O [131]. The other major peaks in the survey scan are attributed to Silicon, Carbon and Oxygen as expected for CNT-ZnO-PDA.

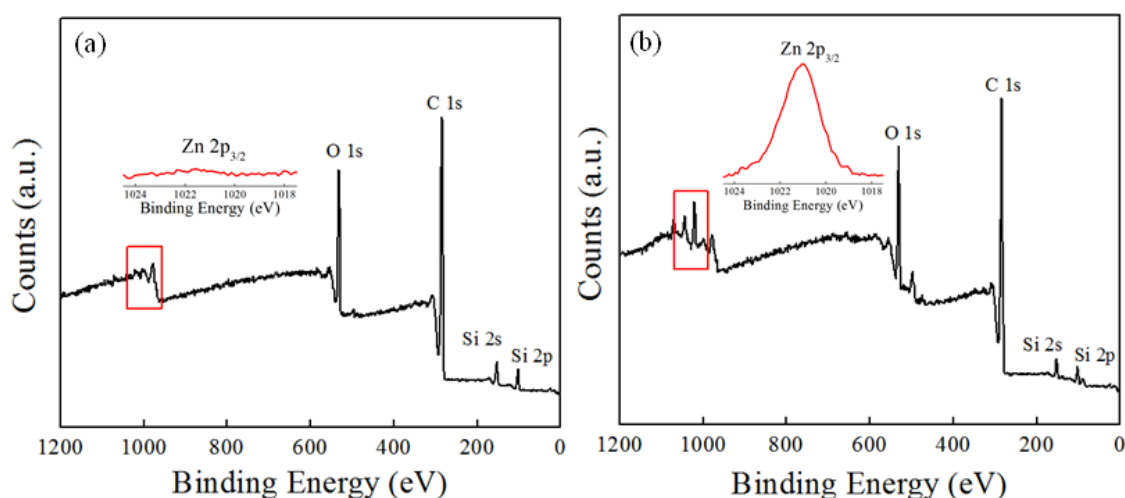


Figure 7.9 (a) XPS survey scan of CNT-ZnO-PDA hybrid before current flow and (b) after current flow. The insets show the Zn $2p_{3/2}$ peaks corresponding to ZnO.

Before current flow, only a very low contribution of ZnO could be observed (Figure 7.9a). This confirms that the ZnO nanoparticles were sandwiched between the MWCNTs and PDA layers. Interestingly, we observe that after current flow, the contribution of Zn 2p_{3/2} increased significantly (Figure 7.9b). It should be noted that the red phase investigated with XPS was formed with a potential of 20 V, much higher than the critical transition voltage of the hybrid (~7 V). It would be meaningless to associate this increase to an increase in ZnO content in the red phase, as the concentration of ZnO was maintained at 5 % by volume for all samples used. As we expect current flow to initiate re-alignment of PDA, it is likely that heavy current flow through CNT-ZnO-PDA hybrids results in a structure where more of the ZnO surface is exposed to the incoming X-rays, explaining the intense Zn 2p_{3/2} peak.

7.8 Does ZnO alter band gap in the hybrid?

The absorbance behavior of a material is indicative of its band gap (E_g). In general, materials that absorb in the red region of the visible spectrum have lower E_g than those that absorb in the blue region. The absorbance peak around 650 nm for PDA in the blue phase is thus indicative of a low E_g while current induced red phase of PDA absorbs in the blue region, suggesting a wider E_g . The numerical quantification of the exact values of band gaps in PDA is not straight forward and is beyond the scope of this work.

The key point to be grasped is that absorbance changes can be used as an estimator of E_g variations in PDA. With this understanding, we noticed that the peak absorbances of the blue phase of CNT-ZnO-PDA hybrid blue shifted by ~20 nm, which points towards a wider E_g than conventional CNT-PDA composites (Figure 7.10). Hence, to initiate the blue to red electrochromic change in these hybrids, one would expect a lower potential difference to be sufficient, as the starting E_g in blue phase is

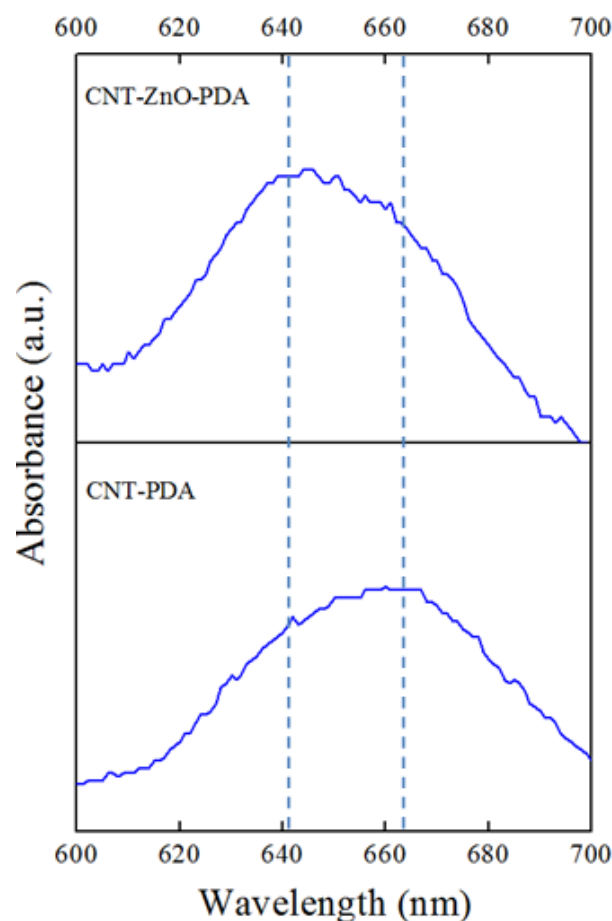


Figure 7.10 Comparison of the absorbance peak shifts in the blue phase of conventional CNT-PDA and CNT-ZnO-PDA hybrids.

closer in value to the red phase when compared to conventional CNT-PDA. This is indeed the case, with CNT-ZnO-PDA hybrid responding electrochromically at ~ 7 V as opposed to 10 V and higher for CNT-PDA composites (Figure 7.5a and 6.6).

7.9 Summary

The effect of incorporating ZnO nanoparticles into CNT-PDA on the electrochromism of the resulting hybrid was investigated. In-situ absorption studies with voltage revealed a critical transition voltage of 7 V and significant recovery of the blue phase upon removal of voltage. XPS analysis of the hybrid prior to current flow showed only a low contribution of ZnO, implying the ZnO nanoparticles were sandwiched between the MWCNT and PDA. In-situ Raman point spectra revealed nearly complete

recovery of peak intensity upon voltage removal, suggesting reversible changes in PDA alignment. The reversibility was further confirmed by comparing Raman maps over a relatively large area, wherein the hybrid gave almost identical maps before and after current flow while conventional CNT-PDA underwent drastic, permanent changes. It is proposed that ZnO plays two roles towards improving electrochromism in CNT-ZnO-PDA hybrids: (i) it widens the band gap of the blue phase resulting in lower critical current for electrochromism and (ii) encourages PDA to revert to initial alignment upon stimulus removal by facilitating ionic head group-ZnO surface interactions.

Chapter 8 Conclusions and future work

8.1 Conclusions

Electrochromism in CNT-PDA composites was found to originate from 3D electron hopping induced de-stacking of PDA orbitals. Moreover, unlike the red phase resulting from the intrinsic stimuli response of PDA, electrically induced red phase of CNT-PDA need not have a stressed structure. This was confirmed by comparing electrochromism in both partially and highly polymerized composites where only the latter gave stress induced shifts in the in-situ Raman spectra. As polarized Raman experiments revealed that PDA realigned along CNTs after current flow, it was evident that a stressed structure is a direct consequence of the extent of polymerization of DA and not necessarily the cause of the color change in PDA as previously understood.

The effects of pre and post polymerization heating on the electrochromism in CNT-PDA composites were investigated and it was found that heat treatment in general increased the V_C in these composites, with the highest transition voltage (16 V) observed for pre heated samples. Raman mapping and in-situ spectral transition dynamics were used to attribute the increased V_C in the pre heated composites to a structure with high degree of stacking, brought about by DA monomers intercalating the gaps between CNT bundles prior to polymerization. By varying pre-heating temperature, it was possible to prepare CNT-PDA composites that could switch from blue to red at voltages ranging from 9-16 V.

CNT-ZnO-PDA hybrids where PDA was anchored onto the surface of ZnO significantly improved recovery of the blue phase upon removal of voltage. In-situ Raman and Raman maps before and after current flow through the hybrids confirmed the enhanced recovery of PDA alignment upon stimulus removal in the hybrid. The

improved electrochromism in the hybrids is likely due to a blue phase with wider band gap than conventional CNT-PDAs and an increased tendency of anchored PDA chains to revert to its initial alignment upon removal of voltage.

8.2 Future work

So far, only non-covalently functionalized CNT-PDA composites have been explored for electrochromism. Though covalent functionalization hampers conductivity in individual CNTs, it has been shown to improve hopping conductivity in CNT macroscopic assemblies (fibers and sheets). Hence, investigating electrochromism of CNT-PDA composites in which the PDA is covalently bonded to the surface of CNTs seems interesting.

The easy control over physical attributes of CNT sheets (width and thickness) and the ease of transfer on to a variety of substrates can be used to create electrochromic origami structures.

Through straight forward design, two CNT-PDA sheets can be stacked at different angles with respect to the substrate. By providing electrical contacts at each of the 4 sheet ends, one can control the direction of current flow in the system. It will be interesting to use the techniques adapted in this research (in-situ Raman and Raman mapping) to investigate how current flow influences PDA alignment in those regions where the sheets overlap. Such work will be useful for practical applications based on weaving high strength electrochromic fabrics with this material.

References

- [1] Bamfield P, Hutchings MG. Chromic Phenomena: Technological Applications of Colour Chemistry, Second Edition: Royal Society of Chemistry; 2010.
- [2] Day JH. Thermochromism. Chemical Reviews. 1963;63(1):65-80.
- [3] Seeboth A, Yin C, Kriwanek J, Lotzsch D, Schaper R. Thermochromic polyolefin foils. Journal of Applied Polymer Science. 2005;96(5):1789-1792.
- [4] Irie M. Diarylethenes for memories and switches. Chemical Reviews. 2000;100(5):1685-1716.
- [5] Hutchings MG, Gregory P, Campbell JS, Strong A, Zamy JP, Lepre A, et al. The comparative solvatochromism of arylazo and heteroarylazo compounds based on N,N-diethyl-m-acetylaminoaniline and N,N-diethyl-m-toluidine. Chemistry - A European Journal. 1997;3(10):1719-1727.
- [6] Monk PMS. Electrochromism: Fundamentals and Applications. Weinheim: VCH; 1995.
- [7] Mortimer RJ. Electrochromic materials. Chemical Society Reviews. 1997;26(3):147-156.
- [8] Kim JM, Lee JS, Choi H, Sohn D, Ahn DJ. Rational design and in-situ FTIR analyses of colorimetrically reversible polydiacetylene supramolecules. Macromolecules. 2005;38(22):9366-9376.
- [9] Peng HS, Sun XM, Cai FJ, Chen XL, Zhu YC, Liao GP, et al. Electrochromatic carbon nanotube/polydiacetylene nanocomposite fibres. Nature Nanotechnology. 2009;4(11):738-741.
- [10] Sun XM, Chen T, Huang SQ, Li L, Peng HS. Chromatic polydiacetylene with novel sensitivity. Chemical Society Reviews. 2010;39(11):4244-4257.

- [11] Yoon B, Lee S, Kim JM. Recent conceptual and technological advances in polydiacetylene-based supramolecular chemosensors. *Chemical Society Reviews*. 2009;38(7):1958-1968.
- [12] Wegner G. Topochemical Reactions of Monomers with Conjugated Triple Bonds .I. Polymerization of 2,4-Hexadiyn-1,6-Diols Deivatives in Crystalline State. *Zeitschrift für Naturforschung B*. 1969;B 24(7):824-828.
- [13] Lauher JW, Fowler FW, Goroff NS. Single-crystal-to-single-crystal topochemical polymerizations by design. *Accounts of Chemical Research*. 2008;41(9):1215-1229.
- [14] Patel GN, Chance RR, Witt JD. Visual Conformational Transition in a Polymer-Solution. *Journal of Polymer Science Part C-Polymer Letters*. 1978;16(11):607-614.
- [15] Chance RR, Shand ML, Hogg C, Silbey R. 3-Wave Mixing in Conjugated Polymer-Solutions - 2-Photon Absorption in Polydiacetylenes. *Physical Review B*. 1980;22(8):3540-3550.
- [16] Lim KC, Heeger AJ. Spectroscopic and Light-Scattering Studies of the Conformational (Rod-to-Coil) Transition of Poly(Diacetylene) in Solution. *J Chemical Physics*. 1985;82(1):522-530.
- [17] Patel GN, Witt JD, Khanna YP. Thermochromism in Polydiacetylene Solutions. *Journal of Polymer Science and Polymer Physics*. 1980;18(6):1383-1391.
- [18] Wenz G, Muller MA, Schmidt M, Wegner G. Structure of Poly(Diacetylenes) in Solution. *Macromolecules*. 1984;17(4):837-850.
- [19] Muller MA, Schmidt M, Wegner G. A Single-Chain Rod-to-Coil Transition of a Conjugated Polymer in Solution - Caveat Emptor. *Macromolecular Rapid Communications*. 1984;5(2):83-88.

- [20] Patel GN, Chance RR, Witt JD. Planar-Nonplanar Conformational Transition in Conjugated Polymer-Solutions. The Journal of Chemical Physics. 1979;70(9):4387-4392.
- [21] Shand ML, Chance RR, Lepostollec M, Schott M. Raman Photoselection and Conjugation-Length Dispersion in Conjugated Polymer-Solutions. Physical Review B. 1982;25(7):4431-4436.
- [22] Lim KC, Kapitulnik A, Zacher R, Heeger AJ. Conformation of Polydiacetylene Macromolecules in Solution - Field-Induced Birefringence and Rotational Diffusion Constant. The Journal of Chemical Physics. 1985;82(1):516-521.
- [23] Bredas JL, Silbey R. Conjugated Polymers: The Novel Science and Technology of Highly Conducting and Nonlinear Optically Active Materials. Dordrecht: Kluwer Academic Publishers; 1991.
- [24] Rawiso M, Aime JP, Fave JL, Schott M, Muller MA, Schmidt M, et al. Solutions of Polydiacetylenes in Good and Poor Solvents - a Light and Neutron-Scattering Study. The Journal of Physics-Paris. 1988;49(5):861-880.
- [25] Ginder JM, Epstein AJ. Role of Ring Torsion Angle in Polyaniline - Electronic-Structure and Defect States. Physical Review B. 1990;41(15):10674-10685.
- [26] Soos ZG, Schweizer KS. Conformational Dependence of Transition Moments in Conjugated Polymers. Abstracts of Papers of the American Chemical Society. 1987;193:86.
- [27] Surjan PR, Kuzmany H. Interruption of Conjugations of Polyacetylene Chains. Physical Review B. 1986;33(4):2615-2624.
- [28] Wenz G, Wegner G. Molecular-Weight Distribution and Solution Properties of a Poly(Diacetylene). Macromolecular Rapid Communications. 1982;3(4):231-237.

- [29] Aime JP, Bargain F. Comments on the Chain Conformation of Conjugated Polymers in Solution. *Europhysics Letters*. 1989;9(1):35-40.
- [30] Bredas JL, Heeger AJ. Theoretical Investigation of Gas-Phase Torsion Potentials Along Conjugated Polymer Backbones - Polyacetylene, Polydiacetylene, and Polythiophene. *Macromolecules*. 1990;23(4):1150-1156.
- [31] Schweizer KS. Order-Disorder Transitions of Pi-Conjugated Polymers in Condensed Phases .1. General-Theory. *The Journal of Chemical Physics*. 1986;85(2):1156-1175.
- [32] Kaplan IG. *Theory of Molecular Interactions*. Netherlands: Elsevier; 1986.
- [33] Haugh EF, Hirschfelder JO. Pi-Electron Forces between Conjugated Double Bond Molecules. *The Journal of Chemical Physics*. 1955;23(10):1778-1796.
- [34] Charoenthai N, Pattanatornchai T, Wacharasindhu S, Sukwattanasinitt M, Traiphol R. Roles of head group architecture and side chain length on colorimetric response of polydiacetylene vesicles to temperature, ethanol and pH. *Journal of Colloid and Interface Science*. 2011;360(2):565-573.
- [35] Lifshitz Y, Golan Y, Konovalov O, Berman A. Structural Transitions in Polydiacetylene Langmuir Films. *Langmuir*. 2009;25(8):4469-4477.
- [36] Kew SJ, Hall EAH. pH response of carboxy-terminated colorimetric polydiacetylene vesicles. *Analytical Chemistry*. 2006;78(7):2231-2238.
- [37] Exarhos GJ, Risen WM, Baughman RH. Resonance Raman Study of Thermochromic Phase-Transition of a Polydiacetylene. *Journal of American Chemical Society*. 1976;98(2):481-487.
- [38] Ye Q, You X, Zou G, Yu XW, Zhang QJ. Morphology, structure and chromatic properties of azobenzene-substituted polydiacetylene supramolecular assemblies. *Journal of Materials Chemistry*. 2008;18(24):2775-2780.

- [39] Lim JK, Lee Y, Lee K, Gong M, Joo SW. Reversible thermochromic change of molecular architecture for a diacetylene derivative 10,12-pentacosadiynoic acid self-assembled thin films on Ag surfaces. *Chemical Letters*. 2007;36(10):1226-1227.
- [40] Jonas U, Shah K, Norvez S, Charych DH. Reversible color switching and unusual solution polymerization of hydrazide-modified diacetylene lipids. *Journal of American Chemical Society*. 1999;121(19):4580-4588.
- [41] Sung XM, Chen T, Huang SQ, Cai FJ, Chen XL, Yang ZB, et al. UV-Induced Chromatism of Polydiacetylenic Assemblies. *Journal of Physical Chemistry B*. 2010;114(7):2379-2382.
- [42] Hammond PT, Rubner MF. Thermochromism in liquid crystalline polydiacetylenes. *Macromolecules*. 1997;30(19):5773-5782.
- [43] Peng HS, Tang J, Pang JB, Chen DY, Yang L, Ashbaugh HS, et al. Polydiacetylene/silica nanocomposites with tunable mesostructure and thermochromatism from diacetylenic assembling molecules. *Journal of American Chemical Society*. 2005;127(37):12782-12783.
- [44] Peng HS, Tang J, Yang L, Pang JB, Ashbaugh HS, Brinker CJ, et al. Responsive periodic mesoporous polydiacetylene/silica nanocomposites. *Journal of American Chemical Society*. 2006;128(16):5304-5305.
- [45] Song J, Cisar JS, Bertozzi CR. Functional self-assembling bolaamphiphilic polydiacetylenes as colorimetric sensor scaffolds. *Journal of American Chemical Society*. 2004;126(27):8459-8465.
- [46] Ahn DJ, Chae EH, Lee GS, Shim HY, Chang TE, Ahn KD, et al. Colorimetric reversibility of polydiacetylene supramolecules having enhanced hydrogen-

- bonding under thermal and pH stimuli. *Journal of American Chemical Society*. 2003;125(30):8976-8977.
- [47] Huang X, Jiang SG, Liu MH. Metal ion modulated organization and function of the Langmuir-Blodgett films of amphiphilic diacetylene: Photopolymerization, thermochromism, and supramolecular chirality. *Journal of Physical Chemistry B*. 2005;109(1):114-119.
- [48] Patlolla A, Zunino J, Frenkel AI, Iqbal Z. Thermochromism in polydiacetylene-metal oxide nanocomposites. *Journal of Materials Chemistry*. 2012;22(14):7028-7035.
- [49] Popov VN. Carbon nanotubes: properties and application. *Materials Science and Engineering Reports*. 2004;43(3):61-102.
- [50] Kroto HW, Heath JR, O'Brien SC, Curl RF, Smalley RE. C-60 - Buckminsterfullerene. *Nature*. 1985;318(6042):162-163.
- [51] Iijima S. Helical Microtubules of Graphitic Carbon. *Nature*. 1991;354(6348):56-58.
- [52] Iijima S, Ichihashi T. Single-Shell Carbon Nanotubes of 1-Nm Diameter. *Nature*. 1993;363(6430):603-605.
- [53] Hirsch A, Brettreich M. Fullerenes: Chemistry and Reactions. Weinheim: Wiley-VCH Verlag GmbH; 2005.
- [54] Lu X, Chen ZF. Curved Pi-conjugation, aromaticity, and the related chemistry of small fullerenes (< C-60) and single-walled carbon nanotubes. *Chemical Reviews*. 2005;105(10):3643-3696.
- [55] Ajayan PM, Stephan O, Colliex C, Trauth D. Aligned Carbon Nanotube Arrays Formed by Cutting a Polymer Resin-Nanotube Composite. *Science*. 1994;265(5176):1212-1214.

- [56] Li WZ, Xie SS, Qian LX, Chang BH, Zou BS, Zhou WY, et al. Large-scale synthesis of aligned carbon nanotubes. *Science*. 1996;274(5293):1701-1703.
- [57] Ren ZF, Huang ZP, Xu JW, Wang JH, Bush P, Siegal MP, et al. Synthesis of large arrays of well-aligned carbon nanotubes on glass. *Science*. 1998;282(5391):1105-1107.
- [58] Fan SS, Chapline MG, Franklin NR, Tomblor TW, Cassell AM, Dai HJ. Self-oriented regular arrays of carbon nanotubes and their field emission properties. *Science*. 1999;283(5401):512-514.
- [59] Jiang KL, Li QQ, Fan SS. Nanotechnology: Spinning continuous carbon nanotube yarns - Carbon nanotubes weave their way into a range of imaginative macroscopic applications. *Nature*. 2002;419(6909):801-803.
- [60] Kuznetsov AA, Fonseca AF, Baughman RH, Zakhidov AA. Structural Model for Dry-Drawing of Sheets and Yarns from Carbon Nanotube Forests. *Acs Nano*. 2011;5(2):985-993.
- [61] Li QW, Li Y, Zhang XF, Chikkannanavar SB, Zhao YH, Dangelewicz AM, et al. Structure-dependent electrical properties of carbon nanotube fibers. *Advanced Materials*. 2007;19(20):3358-3363.
- [62] Lu WB, Zu M, Byun JH, Kim BS, Chou TW. State of the Art of Carbon Nanotube Fibers: Opportunities and Challenges. *Advanced Materials*. 2012;24(14):1805-1833.
- [63] Hirsch A, Vostrowsky O. Functionalization of carbon nanotubes. *Topics in Current Chemistry*. 2005;245:193-237.
- [64] Bahr JL, Mickelson ET, Bronikowski MJ, Smalley RE, Tour JM. Dissolution of small diameter single-wall carbon nanotubes in organic solvents? *Chemical communications*. 2001(2):193-194.

- [65] Hamwi A, Alvergnat H, Bonnamy S, Beguin F. Fluorination of carbon nanotubes. *Carbon*. 1997;35(6):723-728.
- [66] Nakajima T, Kasamatsu S, Matsuo Y. Synthesis and characterization of fluorinated carbon nanotube. *European Journal of Solid State Inorganic Chemistry*. 1996;33(9):831-840.
- [67] Bahr JL, Yang JP, Kosynkin DV, Bronikowski MJ, Smalley RE, Tour JM. Functionalization of carbon nanotubes by electrochemical reduction of aryl diazonium salts: A bucky paper electrode. *Journal of American Chemical Society*. 2001;123(27):6536-6542.
- [68] Tagmatarchis N, Georgakilas V, Prato M, Shinohara H. Sidewall functionalization of single-walled carbon nanotubes through electrophilic addition. *Chemical communications*. 2002(18):2010-2011.
- [69] Basiuk EV, Monroy-Pelaez M, Puente-Lee I, Basiuk VA. Direct solvent-free amination of closed-cap carbon nanotubes: A link to fullerene chemistry. *Nano Letters*. 2004;4(5):863-866.
- [70] Lu X, Tian F, Feng YB, Xu X, Wang NQ, Zhang QN. Sidewall oxidation and complexation of carbon nanotubes by base-catalyzed cycloaddition of transition metal oxide: A theoretical prediction. *Nano Letters*. 2002;2(11):1325-1327.
- [71] Mawhinney DB, Naumenko V, Kuznetsova A, Yates JT, Liu J, Smalley RE. Infrared spectral evidence for the etching of carbon nanotubes: Ozone oxidation at 298 K. *Journal of American Chemical Society*. 2000;122(10):2383-2384.
- [72] Guldi DM, Martin N. *Carbon Nanotubes and Related Structures: Synthesis, Characterization, Functionalization and Applications.*: WILEY-VCH Verlag GmbH & Co.; 2010.

- [73] Tasis D, Tagmatarchis N, Bianco A, Prato M. Chemistry of carbon nanotubes. *Chemical Reviews*. 2006;106(3):1105-1136.
- [74] Britz DA, Khlobystov AN. Noncovalent interactions of molecules with single walled carbon nanotubes. *Chemical Society Reviews*. 2006;35(7):637-659.
- [75] Eswaramoorthy M, Sen R, Rao CNR. A study of micropores in single-walled carbon nanotubes by the adsorption of gases and vapors. *Chemical Physics Letters*. 1999;304(3-4):207-210.
- [76] Weber SE, Talapatra S, Journet C, Zambano Z, Migone AD. Determination of the binding energy of methane on single-walled carbon nanotube bundles. *Physical Review B*. 2000;61(19):13150-13154.
- [77] Zambano AJ, Talapatra S, Migone AD. Binding energy and monolayer capacity of Xe on single-wall carbon nanotube bundles. *Physical Review B*. 2001;64(7).
- [78] Sumanasekera GU, Pradhan BK, Romero HE, Adu KW, Eklund PC. Giant thermopower effects from molecular physisorption on carbon nanotubes. *Physical Review Letters*. 2002;89(16).
- [79] Moore VC, Strano MS, Haroz EH, Hauge RH, Smalley RE, Schmidt J, et al. Individually suspended single-walled carbon nanotubes in various surfactants. *Nano Letters*. 2003;3(10):1379-1382.
- [80] O'Connell MJ, Bachilo SM, Huffman CB, Moore VC, Strano MS, Haroz EH, et al. Band gap fluorescence from individual single-walled carbon nanotubes. *Science*. 2002;297(5581):593-596.
- [81] Wenseleers W, Vlasov II, Goovaerts E, Obraztsova ED, Lobach AS, Bouwen A. Efficient isolation and solubilization of pristine single-walled nanotubes in bile salt micelles. *Advanced Functional Materials*. 2004;14(11):1105-1112.

- [82] O'Connell MJ, Boul P, Ericson LM, Huffman C, Wang YH, Haroz E, et al. Reversible water-solubilization of single-walled carbon nanotubes by polymer wrapping. *Chemical Physics Letters*. 2001;342(3-4):265-271.
- [83] McCarthy B, Coleman JN, Czerw R, Dalton AB, Panhuis MIH, Maiti A, et al. A microscopic and spectroscopic study of interactions between carbon nanotubes and a conjugated polymer. *Journal of Physical Chemistry B*. 2002;106(9):2210-2216.
- [84] Ago H, Shaffer MSP, Ginger DS, Windle AH, Friend RH. Electronic interaction between photoexcited poly(p-phenylene vinylene) and carbon nanotubes. *Physical Reviews B*. 2000;61(3):2286-2290.
- [85] Yang MJ, Koutsos V, Zaiser M. Interactions between polymers and carbon nanotubes: A molecular dynamics study. *Journal of Physical Chemistry B*. 2005;109(20):10009-10014.
- [86] Blythe T, Bloor D. *Electrical Properties of Polymers*, 2 ed. New York: Cambridge University Press; 2005.
- [87] Yu SF, Zhou HL, He PS. X-ray diffraction analysis of 10,12-pentacosadiynoic acid Langmuir-Blodgett films during polymerization. *Journal of Materials Science*. 1999;34(13):3149-3154.
- [88] Zhang M, Fang SL, Zakhidov AA, Lee SB, Aliev AE, Williams CD, et al. Strong, transparent, multifunctional, carbon nanotube sheets. *Science*. 2005;309(5738):1215-1219.
- [89] Di JT, Hu DM, Chen HY, Yong ZZ, Chen MH, Feng ZH, et al. Ultrastrong, Foldable, and Highly Conductive Carbon Nanotube Film. *Acs Nano*. 2012;6(6):5457-5464.

- [90] Fu WQ, Liu L, Jiang KL, Li QQ, Fan SS. Super-aligned carbon nanotube films as aligning layers and transparent electrodes for liquid crystal displays. *Carbon*. 2010;48(7):1876-1879.
- [91] Liu P, Liu L, Wei Y, Liu K, Chen Z, Jiang KL, et al. Fast High-Temperature Response of Carbon Nanotube Film and Its Application as an Incandescent Display. *Advanced Materials*. 2009;21(35):3563-3567.
- [92] Liu W, Zhang XH, Xu G, Bradford PD, Wang X, Zhao HB, et al. Producing superior composites by winding carbon nanotubes onto a mandrel under a poly(vinyl alcohol) spray. *Carbon*. 2011;49(14):4786-4791.
- [93] Naseh MV, Khodadadi AA, Mortazavi Y, Pourfayaz F, Alizadeh O, Maghrebi M. Fast and clean functionalization of carbon nanotubes by dielectric barrier discharge plasma in air compared to acid treatment. *Carbon*. 2010;48(5):1369-1379.
- [94] Pohls JH, Johnson MB, White MA, Malik R, Ruff B, Jayasinghe C, et al. Physical properties of carbon nanotube sheets drawn from nanotube arrays. *Carbon*. 2012;50(11):4175-4183.
- [95] Zhang HX, Feng C, Zhai YC, Jiang KL, Li QQ, Fan SS. Cross-Stacked Carbon Nanotube Sheets Uniformly Loaded with SnO₂ Nanoparticles: A Novel Binder-Free and High-Capacity Anode Material for Lithium-Ion Batteries. *Advanced Materials*. 2009;21(22):2299-2303.
- [96] Zhang YY, Sheehan CJ, Zhai JY, Zou GF, Luo HM, Xiong J, et al. Polymer-Embedded Carbon Nanotube Ribbons for Stretchable Conductors. *Advanced Materials*. 2010;22(28):3027-3031.
- [97] Chance RR, Baughman RH, Muller H, Eckhardt CJ. Thermochromism in a Polydiacetylene Crystal. *Journal of Chemical Physics*. 1977;67(8):3616-3618.

- [98] Muller H, Eckhardt CJ. Stress-Induced Change of Electronic-Structure in a Polydiacetylene Crystal. *Molecular Crystals and Liquid Crystals*. 1978;45(3-4):313-318.
- [99] Day D, Hub HH, Ringsdorf H. Polymerization of Mono-Functional and Bi-Functional Diacetylene Derivatives in Monolayers at the Gas-Water Interface. *Israel Journal of Chemistry*. 1979;18(3-4):325-329.
- [100] Tieke B, Lieser G, Wegner G. Polymerization of Diacetylenes in Multilayers. *Journal of Polymer Science and Polymer Chemistry*. 1979;17(6):1631-1644.
- [101] Olmsted J, Strand M. Fluorescence of Polymerized Diacetylene Bilayer Films. *Journal of Physical Chemistry*. 1983;87(24):4790-4792.
- [102] Tomioka Y, Tanaka N, Imazeki S. Surface-Pressure-Induced Reversible Color-Change of a Polydiacetylene Monolayer at a Gas Water Interface. *Journal of Chemical Physics*. 1989;91(9):5694-5700.
- [103] Wenzel M, Atkinson GH. Chromatic Properties of Polydiacetylene Films. *Journal of American Chemical Society*. 1989;111(16):6123-6127.
- [104] Nallicheri RA, Rubner MF. Investigations of the Mechanochromic Behavior of Poly(Urethane Diacetylene) Segmented Copolymers. *Macromolecules*. 1991;24(2):517-525.
- [105] Charych DH. Direct Colorimetric Detection of a Receptor-Ligand Interaction by a Polymerized Bilayer Assembly (Vol 261, Pg 585, 1993). *Science*. 1993;261(5127):1375-.1378
- [106] Reichert A, Nagy JO, Spevak W, Charych D. Polydiacetylene Liposomes Functionalized with Sialic-Acid Bind and Colorimetrically Detect Influenza-Virus. *Journal of American Chemical Society*. 1995;117(2):829-830.

- [107] Charych D, Cheng Q, Reichert A, Kuziemko G, Stroh M, Nagy JO, et al. A 'litmus test' for molecular recognition using artificial membranes. *Chemical Biology*. 1996;3(2):113-120.
- [108] Lio A, Reichert A, Ahn DJ, Nagy JO, Salmeron M, Charych DH. Molecular imaging of thermochromic carbohydrate-modified polydiacetylene thin films. *Langmuir*. 1997;13(24):6524-6532.
- [109] Cheng Q, Stevens RC. Charge-induced chromatic transition of amino acid-derivatized polydiacetylene liposomes. *Langmuir*. 1998;14(8):1974-1976.
- [110] Carpick RW, Mayer TM, Sasaki DY, Burns AR. Spectroscopic ellipsometry and fluorescence study of thermochromism in an ultrathin poly(diacetylene) film: Reversibility and transition kinetics. *Langmuir*. 2000;16(10):4639-4647.
- [111] Singh A, Thompson RB, Schnur JM. Reversible Thermochromism in Photopolymerized Phosphatidylcholine Vesicles. *Journal of American Chemical Society*. 1986;108(10):2785-2787.
- [112] Yuan ZZ, Lee CW, Lee SH. Reversible thermochromism in hydrogen-bonded polymers containing polydiacetylenes. *Angewandte Chemical International Edition*. 2004;43(32):4197-4200.
- [113] Gu Y, Cao WQ, Zhu L, Chen DY, Jiang M. Polymer mortar assisted self-assembly of nanocrystalline polydiacetylene bricks showing reversible thermochromism. *Macromolecules*. 2008;41(7):2299-2303.
- [114] Ahn DJ, Lee S, Kim JM. Rational Design of Conjugated Polymer Supramolecules with Tunable Colorimetric Responses. *Advanced Functional Materials*. 2009;19(10):1483-1496.

- [115] Potisatityuenyong A, Rojanathanes R, Turncharern G, Sukwattanasinitt M. Electronic absorption spectroscopy probed side-chain movement in chromic transitions of polydiacetylene vesicles. *Langmuir*. 2008;24(9):4461-4463.
- [116] Seto K, Hosoi Y, Furukawa Y. Raman spectra of Langmuir-Blodgett and Langmuir-Schaefer films of polydiacetylene prepared from 10,12-pentacosadiynoic acid. *Chemical Physics Letters*. 2007;444(4-6):328-332.
- [117] Kim JM, Lee YB, Chae SK, Ahn DJ. Patterned color and fluorescent images with polydiacetylene supramolecules embedded in poly(vinyl alcohol) films. *Advanced Functional Materials*. 2006;16(16):2103-2109.
- [118] Chen YJ, Carter GM, Tripathy SK. Study of Langmuir-Blodgett Polydiacetylene Polymer-Films by Surface Enhanced Raman-Scattering. *Solid State Commun*. 1985;54(1):19-22.
- [119] Dai ZH, Gao Y, Liu LQ, Potschke P, Yang JL, Zhang Z. Creep-resistant behavior of MWCNT-polycarbonate melt spun nanocomposite fibers at elevated temperature. *Polymer*. 2013;54(14):3723-3729.
- [120] Gommans HH, Alldredge JW, Tashiro H, Park J, Magnuson J, Rinzler AG. Fibers of aligned single-walled carbon nanotubes: Polarized Raman spectroscopy. *Journal of Applied Physics*. 2000;88(5):2509-2514.
- [121] Zhong XL, Pandey R, Karna SP. Stacking dependent electronic structure and transport in bilayer graphene nanoribbons. *Carbon*. 2012;50(3):784-790.
- [122] Kaneko F, Shibata M, Kobayashi S. Absorption Properties and Structure Changes Caused by Pre-Annealing in Polydiacetylene Langmuir-Blodgett-Films. *Thin Solid Films*. 1992;210(1-2):548-550.

- [123] Shibata M, Kaneko F, Aketagawa M, Kobayashi S. Reversible Color Phase-Transitions and Annealing Properties of Langmuir-Blodgett Polydiacetylene Films. *Thin Solid Films*. 1989;179:433-437.
- [124] Jimison LH, Salleo A, Chabinyc ML, Bernstein DP, Toney MF. Correlating the microstructure of thin films of poly[5,5-bis(3-dodecyl-2-thienyl)-2,2-bithiophene] with charge transport: Effect of dielectric surface energy and thermal annealing. *Physical Review B*. 2008;78(12).
- [125] Varghese Hansen R, Huang M, Zhan Z, Sun G, Yang J, Zheng L. On the study of electrochromism in multiwalled carbon nanotube–polydiacetylene composites. *Carbon*. 2015;90(0):222-230.
- [126] Chanakul A, Traiphol N, Traiphol R. Controlling the reversible thermochromism of polydiacetylene/zinc oxide nanocomposites by varying alkyl chain length. *Journal of Colloid and Interface Science*. 2013;389:106-114.
- [127] Chanakul A, Traiphol N, Faisadcha K, Traiphol R. Dual colorimetric response of polydiacetylene/Zinc oxide nanocomposites to low and high pH. *Journal of Colloid and Interface Science*. 2014;418:43-51.
- [128] Toommee S, Traiphol R, Traiphol N. High color stability and reversible thermochromism of polydiacetylene/zinc oxide nanocomposite in various organic solvents and polymer matrices. *Colloids and Surfaces A*. 2015;468:252-261.
- [129] Traiphol N, Faisadcha K, Potaib R, Traiphol R. Fine tuning the color-transition temperature of thermoreversible polydiacetylene/zinc oxide nanocomposites: The effect of photopolymerization time. *Journal of Colloid and Interface Science*. 2015;439:105-111.

- [130] Traiphol N, Rungruangviriya N, Potai R, Traiphol R. Stable polydiacetylene/ZnO nanocomposites with two-steps reversible and irreversible thermochromism: The influence of strong surface anchoring. *Journal of Colloid and Interface Science*. 2011;356(2):481-489.
- [131] Alaboson JMP, Sham CH, Kewalramani S, Emery JD, Johns JE, Deshpande A, et al. Templating Sub-10 nm Atomic Layer Deposited Oxide Nanostructures on Graphene via One-Dimensional Organic Self-Assembled Monolayers. *Nano Letters*. 2013;13(12):5763-5770.
- [132] Zhang YN, Zheng LX, Sun GZ, Zhan ZY, Liao K. Failure mechanisms of carbon nanotube fibers under different strain rates. *Carbon* 2012;50(8):2887–2893.
- [133] Zheng LX, Sun GZ, Zhan ZY. Tuning array morphology for high-strength carbon-nanotube fibers. *Small* 2010;6(1):132–137.

Biography

I, Reinack Varghese Hansen, graduated from PSG college of Technology (affiliated to Anna University, India) with a Master's degree in Materials Science in 2010 and enrolled as a PhD student in Nanyang Technological University in August 2011. Skilled in the design and synthesis of functional carbon nanotube-polymer composites, I have significant experience carrying out dry spinning of macroscopic CNT sheet and fiber assemblies followed by functionalization of the same. I have also grown vertically aligned CNTs on various substrates using chemical vapor deposition (CVD) for use as supercapacitor electrodes. I aspire to be part of a research team focused on eco-friendly technology and design based on carbon and carbon-polymer composites.

Academic Highlights

- Certified for Small Group Teaching by NTU, 2013
- Awarded NTU Scholarship to pursue PhD, 2011 - 2015
- Ranked 3rd in class (CGPA 8.2/10) - M.Sc. Materials Science, 2010
- Placed in top 10 % of class - B.Sc. Applied Sciences, 2008

Skills and Capabilities

- Significant experience with the operation protocols of a class 10k/100 Clean Room.
- Experienced at growing drawable CNT forests for dry spinning macroscopic CNT fibers and sheets.
- Familiar with designing and fabricating aligned, macroscopic CNT-polymer functional composites for diverse applications.
- Significant experience using Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), Raman Spectrophotometer and UV-Vis Spectrophotometer. Also familiar with X-ray diffractometry (XRD), X-ray

Photoelectron Spectroscopy (XPS) and Differential Scanning Calorimetry (DSC) analysis.

- Origin, Photoshop, ImageJ, Sketchup, Light Room, MATLAB and Microsoft Office Tools.
- Experienced at growing vertically aligned CNT forest on various substrates for use as supercapacitor electrodes. Also familiar with fabricating hybrid supercapacitors based on horizontally aligned CNT sheets and conducting polymers for flexible electronics.

Publications

- H.V. Reinack, M. Huang, Z. Zhan, G. Sun, L. Zheng, J. Yang, "On The Study Of Electrochromism In Multiwalled Carbon nanotube-Polydiacetylene Composites," 2015, Carbon, Volume: 90, Pages: 222-230.
- X.Z. Tang, Y. Bin, H.V. Reinack, X. Chen, X. Hu, J. Yang, "Grafting Low Contents of Branched Polyethylenimine onto Carbon Fibers to Effectively Improve Their Interfacial Shear Strength with an Epoxy Matrix," 2015, Advanced Materials Interfaces, 1500122.
- J. An, Z. Zhan, S.V.M.K. Hari, G. Sun, H.V. Reinack, L. Zheng, "Trench structure assisted alignment in ultralong and dense carbon nanotube arrays," 2015, Journal of Materials Chemistry C, Volume: 3, Issue: 10, Pages: 2215-2222.
- G. Sun, L. Zheng, Z. Zhan, C. Jiang, H.V. Reinack, Y. Khor, "Highly Reliable Carbon Nanotube-Based Composite Fibers Cross-Linked by a 3D Polymer Network," 2014, Advanced Engineering Materials, Volume: 16, Issue: 8, Pages: 961-965.
- Z. Zhan, J. An, H. Zhang, H. V. Reinack, L. Zheng, "Three-Dimensional Plasmonic Photoanodes Based on Au-Embedded TiO₂ Structures for Enhanced Visible-Light

Water Splitting,” 2014, ACS Applied Materials & Interfaces, Volume: 6, Issue: 2, Pages: 1139-1144.

Conferences

- H.V. Reinack, J. Yang, L. Zheng, “How heat treatment affects the chromatic response of carbon nanotube-polydiacetylene composites to electrical stimulus,” 20th International Conference on Composite Materials, Copenhagen, 2015.
- H.V. Reinack, J. Yang, L. Zheng, “Electrochromism in polydiacetylene-ZnO-carbon nanotube hybrid sheets,” 8th International Conference on Materials for Advanced Technologies of the Materials Research Society of Singapore, 2015.
- H.V. Reinack, J. Yang, L. Zheng, "Electrochromism in polydiacetylene-carbon nanotube composites; a spectroscopic study," poster presented at the 6th MRS-S Conference on Advanced Materials, Singapore, 2014.
- H.V. Reinack, M. Ulaganathan, S. Sreejith, Y. Zhao, L. Zheng, J. Yang, "Multiwall carbon nanotube-polydiacetylene microfibers for supercapacitors," poster presented at Humboldt Kolleg International Symposium on Environment and Health in the 21st Century, Singapore, 2014.